A THESIS

entitled

STUDIES IN THE PYROLYSIS OF FLUORO-OLEFINES AND RELATED COMPOUNDS.

PRESENTED BY

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A.B. [Signature]
ABSTRACT

As a preliminary to the study of the thermal reactions of tetrafluoroethylene, the thermal decomposition of ethylene at 650°C. has been investigated using a flow method. A short account of the thermal reactions of ethylene is given.

The preparation and properties of a number of saturated, unsaturated and cyclic fluorocarbons is surveyed.

The thermal reactions of tetrafluoroethylene have been investigated over the temperature range 300°C to 800°C, by a flow method. Determinations of vapour pressures, melting points and boiling points of the products are reported.

Below 600°C, a simple dimerization of tetrafluoroethylene to octafluorocyclobutane takes place. At temperatures above 600°C, fluorine atom transfers and ring opening occur. The products of pyrolysis at 700°C, contain principally hexafluoropropene and octafluorobutenes. At 800°C, reactions involving the breaking of C-C bonds occur. The free radicals formed react to give low molecular weight saturated, and high molecular weight unsaturated products.

In a study of the kinetics of the reactions occurring at temperatures below 600°C, the dimerization of tetrafluoroethylene to octafluorocyclobutane was found to be reversible. The rate of the forward reaction has been measured at
temperatures between 300° and 550°C., and the rate of the reverse reaction at 520° to 590°C. The dimerization of tetrafluoroethylene is a homogeneous, second order reaction, and the decomposition of octafluorocyclobutane a homogeneous, first order reaction. The energies, heats, and entropies of activation for the forward and reverse reactions have been calculated, and their theoretical significance discussed. The values obtained have been used as a basis for comparison of the reactions under consideration with the corresponding reactions of hydrocarbons.
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INTRODUCTION

Our knowledge of the chemistry of the fluorocarbons has undergone considerable development during the past ten years, mainly because of the exigencies of the war. Most of the activities have been directed towards obtaining new methods of synthesizing fluorocarbons on a practical scale, and improving existing preparative techniques. As a result of this work a number of these compounds are now available in quantity. Up to the present little work has been done on the physical chemistry of these compounds, and large gaps exist in any tables of their physical properties.

The work described in this thesis was carried out with a view to obtaining further data on the reactivity and physical properties of the simpler fluorocarbons. It can briefly be described as a study of the kinetics of the thermal decomposition of tetrafluoroethylene and of the properties of the products formed. Besides providing knowledge of general interest, it was hoped that the information derived from the investigation would assist in extending the work done at Imperial College on the mercury photosensitized reaction of tetrafluoroethylene (1). Some of the products of the latter reaction are obtained in very low yield, and there is little hope of identifying them until the properties
of aliphatic fluorocarbons are more fully catalogued.

Before proceeding to the investigation of the thermal decomposition of tetrafluoroethylene it was decided to test the efficiency of the apparatus constructed and to acquire a technique of operation by studying briefly the thermal decomposition of an easily obtainable gaseous compound. To this end, the pyrolysis of ethylene was investigated at 650°C, by a flow method. A description of this preliminary work is given in Part I of the thesis. A short review of the published work on the thermal decomposition of ethylene is also included in this section. The data given in this review formed a useful basis for the discussion of the results obtained from the investigation of the thermal decomposition of tetrafluoroethylene.

A description of the investigation of the products formed by the thermal decomposition of tetrafluoroethylene is given in Part II of the thesis. Certain physical properties of the products of pyrolysis have been measured, and the data obtained is given in this section.

Comprehensive reviews of organic fluorine compounds have been published by Simons (2) and by Smith (3). Also a considerable proportion of the published work is described or reviewed in the reports of the American Chemical Society symposium on fluorine chemistry (4), and the National Nuclear Energy Series publication (5). The literature survey
given in Part II is therefore limited to an account of the properties of the simpler fluorocarbons which are of interest in connection with the present work.

The results obtained from the work described in Part II show that below 600°C, the only reaction occurring is the dimerization of tetrafluoroethylene to give octafluorocyclobutane.

Part III of this thesis contains an account of the more detailed study of the dimerization reaction, which was carried out with a view to obtaining accurate kinetic data. The reaction was found to be reversible, and a study of the kinetics of the reverse reaction is also reported in Part III.

The results obtained from the work described in Parts II and III are discussed in Part IV of the thesis. A comparison has been made between the dimerization reactions of ethylene and tetrafluoroethylene, and between the decomposition reactions of cyclobutane and octafluorocyclobutane.
PART I: THE THERMAL DECOMPOSITION OF ETHYLENE

1. INTRODUCTION.

(a) The purpose of the work.

Before proceeding to the study of the thermal decomposition of tetrafluoroethylene by the flow method, it was decided to carry out a brief investigation of the thermal decomposition of a similar gaseous compound by the same method. The investigation was carried out solely with a view to acquiring a technique of operation of the flow system, and of analysis of the products of pyrolysis by low temperature fractional distillation and by gas analysis. This preliminary work was very necessary as only a limited supply of tetrafluoroethylene was available.

The gas chosen for this work was ethylene, because of its ready availability and also because of its similarity to tetrafluoroethylene. This choice was additionally suitable since the thermal decomposition of ethylene has been exhaustively studied by a number of workers. The results obtained in these investigations were used both to check the validity of the results obtained in the experiments described below, and also for a basis of discussion of the results obtained from the investigation of the thermal decomposition of tetrafluoroethylene.
(b) **The thermal reactions of ethylene.**

(i) **Introduction.**

An examination of the literature on the thermal reactions of ethylene shows that the data available provide detailed information on the reactions occurring over a wide range of temperature. The subject has been extensively reviewed by a number of authors (6)(7)(8). Only a brief survey will therefore be presented here, together with an outline of the mechanisms postulated to account for the numerous products of thermal decomposition.

Broadly speaking, ethylene undergoes two types of reactions when heated, decomposition and polymerization. At low temperatures and high pressures polymerization predominates, whereas mainly decomposition reactions occur at high temperatures and low pressures. In the following review, the investigation of the thermal decomposition of ethylene at low, medium, and high temperatures have, for convenience, been considered separately. This treatment may tend to give an oversimplified picture of the reactions occurring under various conditions. It must be borne in mind therefore that at all temperatures the principal reactions occurring are accompanied by various side reactions, and that no temperature regions exist in which only decomposition reactions or polymerization reactions occur.
(ii) **Low temperature reactions.**

The polymerization of ethylene has been studied by Pease (9)(10) at low temperatures and high pressures. Under these conditions ethylene polymerizes to give higher mono-olefines. Decomposition reactions were not entirely eliminated, and small amounts of methane, ethane, and hydrogen were also obtained. The proportions of these decomposition products increased with temperature and reaction time. Pease carried out a series of experiments in which ethylene was heated in a copper bomb at 350° to 500°C. and at initial pressures of 2.5, 5, and 10 atmospheres. He concluded from his results that butylene was the primary product of reaction, and he obtained a value of 35 k.cal. for the energy of activation of the reaction

\[ 2C_2H_4 = C_4H_8 \]  

(1)

In calculating this result, Pease assumed that the primary reaction occurring was a second order reaction and he neglected the small effect of decomposition reactions. His value is in close agreement with the most recent figure of 34.6 k.cal. obtained by Molera and Stubbs (11). Pease concluded that the high molecular weight olefines obtained from the polymerization of ethylene at low temperatures and high pressures, were formed by reactions of the type
\[ C_2H_4 + C_4H_8 = C_6H_{12} \] (2)
\[ C_6H_{12} + C_2H_4 = C_8H_{16} \] (3)

(iii) High temperature reactions.

The thermal decomposition of ethylene at very high temperatures and low pressures has been studied by Tropsch, Parrish, and Eglof (12). They found that when ethylene was heated at 1100°C. and 1400°C. and at 50mm. pressure for periods of time varying between 0.0007 and 0.044 sec., the principal products of reaction were acetylene and hydrogen. This indicates that under the above conditions the main primary reaction occurring is the decomposition reaction

\[ C_2H_4 = C_2H_2 + H_2 \] (4)

Schneider and Frolich (13) found that at 725°C. and 150 mm. pressure, for every 100 molecules of ethylene reacting, about 41 molecules of hydrogen, 36 molecules of butadiene, 12 molecules of propylene, and 3 molecules of butylene were formed. From these results it was concluded that the main primary reaction occurring was

\[ 2C_2H_4 = C_4H_6 + H_2 \] (5)

The results obtained by earlier workers (14)(15) also indicate that at this temperature butadiene is a prominent product of reaction. Zanetti et al. (14) observed that on heating ethylene at atmospheric pressure, the
maximum yield of butadiene was obtained at 750°C.

The following alternative mechanism was suggested by Burke, Baldwin, and Whitacre (8),

\[
C_2H_4 = C_2H_2 + H_2 \quad (6)
\]

\[
C_2H_4 + C_2H_2 = C_4H_6 \quad (7)
\]

This mechanism for the formation of butadiene was considered to be more consistent with the overall reaction order of between 1 and 2 found by these authors. They were unable to find any more than a trace of acetylene among the products of pyrolysis of ethylene at 625°C., and 1 atmosphere pressure. This was considered to be due to the high reactivity of the acetylene formed by reaction (6). It was found that on adding small amounts of acetylene to the ethylene before pyrolysis, \(72\) to \(97.5\%\) of the acetylene added reacted giving a slight increase in the relative amount of liquid products formed. The general distribution of products was, however, remarkably slightly affected.

If reaction (7) occurs readily at 625°C., it is difficult to understand why it does not occur even more readily at 1100°C. and 1400°C. Tropsch, Parrish, and Eglof (12) found only small amounts of butadiene at 1100°C. and the proportion was found to decrease with increasing reaction time. It seems probable therefore that reaction (7) is reversible, the equilibrium lying to the right at 625°C.
and 1 atmosphere pressure and to the left at 1100°C. and 50mm. pressure.

(iv) Medium temperature reactions.

The effect of temperature on the nature of the reactions occurring is shown by the recent work of Molera and Stubbs (11), who heated ethylene in a silica bulb at various temperatures and at an initial pressure of 200mm. They found that at temperatures up to 650°C. a decrease in pressure occurred, indicating that polymerization was taking place. At 700°C. an initial decrease in pressure was followed by an increase, and at higher temperatures only an increase in pressure was observed, indicating that decomposition reactions were predominant.

The rate of polymerization was determined from the slope of the Δp-time curve at several temperatures between 623°C. and 713°C., and the reaction was found to be exactly of the second order over this temperature range. The rate of decomposition as measured by the tangents to the Δp-time curves at higher temperatures, or the tangents where Δp becomes positive for curves of intermediate type, was determined at temperatures between 713°C. and 783°C. with initial pressures of from 50 to 500mm. The reaction was found to be of the first order up to 250mm. pressure, but at higher pressures the order increased towards two. It was
observed that in the temperature region of 700°C, the rates of decomposition and polymerization were nearly equal. These results support the theory that reaction (1) is the principal reaction occurring at low temperatures, and that reaction (4) is the main reaction occurring at low pressures and high temperatures.

The products of pyrolysis of ethylene at 600°C contain appreciable quantities of butylene, butadiene, and hydrogen (8)(16). It may therefore be concluded that both reactions (1) and (4) occur at this temperature.

The principal product of pyrolysis of ethylene at 600°C. and 1 atmosphere pressure is propylene (8)(16). The following mechanism has been suggested for the formation of this compound,

\[ C_4H_8 + C_2H_4 = 2C_3H_6 \]  

(8)

It was found (8) that on diluting the ethylene, the relative amount of propylene obtained decreased. This is consistent with the above explanation for propylene formation. It was also found that the relative proportion of propylene was augmented by addition of a small amount of butene-1 to the ethylene before pyrolysis. This was considered to be further evidence in favour of reaction (8) as the mechanism of formation of propylene.

Appreciable quantities of methane, ethane, and
liquid products are also obtained from the thermal decomposition of ethylene at temperatures in the region of 600°C. and 1 atmosphere pressure (8)(16). Methane and ethane appear to be secondary products formed principally by the decomposition of higher olefines. The thermal reactions of butene-1 have been studied by Hurd and Goldsby (17) who found that at 600°C, the compound decomposes to give appreciable quantities of methane. Frey and Smith (16) found that methane was the principal product of pyrolysis of propylene at 575°C. It seems likely therefore that the methane obtained from the thermal decomposition of ethylene at temperatures in the region of 600°C is a secondary product formed by the decomposition of propylene, butylene, and higher olefines. The ethane obtained from the pyrolysis of ethylene may be formed in a similar manner, or alternatively by the hydrogenation of ethylene,

\[ C_2H_4 + H_2 = C_2H_6 \]  

the hydrogen being formed by reactions such as (4) and (5).

The formation of methane from high molecular weight olefines such as butene-1, must take place by a free radical mechanism. Szware and Sheon (22) studied the pyrolysis of butene-1 in the presence of toluene, by a flow method, over the temperature range 662°C to 773°C. They obtained a value of 62.2 k.cal. for the energy of activation of the
reaction

\[ \text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3 = \text{CH}_2=\text{CH}_2^- + -\text{CH}_3 \]  

(10)

It seems probable, therefore, that butylene formed by the polymerization of ethylene will decompose at temperatures in the region of 700°C. to yield methyl and allyl radicals. The methyl radicals may then react to give methane by abstraction of hydrogen from ethylene or from a higher molecular weight product. The work of Beeck and Rust (23) who investigated the polymerization of ethylene sensitized by lead tetramethyl, suggests that in addition to hydrogen abstraction, the methyl radicals may react with ethylene giving rise to a chain polymerization reaction,

\[ \text{CH}_3^- + \text{C}_2\text{H}_4 = \text{C}_3\text{H}_7^- \text{ etc.} \]  

(11)

The reaction products obtained by Beeck and Rust consisted of paraffins and olefines with carbon numbers from 3 to 6, together with a little methane. The products contained more olefines than paraffins. These results suggest that the formation of large radicals is interrupted by the decomposition of the radicals into olefines and smaller radicals. No hydrogen was found among the products indicating that the higher radicals decomposed by a C-C split eg.

\[ \text{C}_3\text{H}_7^- = \text{CH}_3^- + \text{C}_2\text{H}_4 \]  

(12)
rather than by splitting off a hydrogen,

\[ \text{C}_3\text{H}_7^- = \text{C}_3\text{H}_6 + \text{H}^- \]  

(13)
Eglof, Schad, and Lowry (6) suggested in their review of the earlier work on the decomposition and polymerization reactions of olefinic hydrocarbons, that the primary reaction in the thermal decomposition of ethylene was

\[ C_2H_4 = 2CH_2; \] (14)

followed by

\[ CH_2: + C_2H_4 = C_3H_5; \] (15)

\[ C_3H_5: + C_2H_4 = C_4H_8; \text{ etc.} \] (16)

Calculations carried out using the figures quoted by Leidler and Casey (21) for the dissociation energies of methane and its radicals, show that the approximate energy of activation for (14) is either 120k.cal. or 160k.cal. depending on whether the methyl-radicals formed are in the singlet or triplet states respectively. These values definitely rule out reaction (14) as the primary step in the polymerization of ethylene.

An alternative primary reaction leading to the formation of free radicals which has not hitherto been mentioned is

\[ 2C_2H_4 = CH_3- + -C_3H_5 \] (17)

Taking the value quoted by Swarc and Sheon (22) for the energy of activation of (10) and using values given by the National Bureau of Standards (25) for the heats of formation of ethylene and butene-1,
is obtained approximately $40 \text{k.cal.}$ for the energy of activation of (17). Taking a value of $10 \text{k.cal.}$ for the energy of activation of the reaction

$$C_2H_4 + -R = -R'$$

and assuming that the energy of activation for the recombination of radicals is zero, we obtain a value of $30 \text{k.cal.}$ for the energy of activation of the polymerization reaction. Thus (17) appears to be a possible primary reaction in the polymerization of ethylene. This reaction would be expected to lead to the formation of similar products to those obtained by Beeck and Rust (23) in the sensitized polymerization of ethylene.

(v) The effect of Nitric Oxide on the thermal reactions of ethylene.

The thermal decomposition of ethylene in the presence of nitric oxide has been studied by Burnham and Pease (18), and by Molera and Stubbs (11). The results of these two investigations suggest that radical chain reactions are occurring in the polymerization of ethylene. The experimental results are difficult to interpret however, since secondary effects appear to occur which give rise to conflicting results.

Burnham and Pease observed that at $500^\circ \text{C.}$ and an initial pressure of $713 \text{mm.}$ of ethylene, small amounts of nitric oxide cut down the initial rate of polymerization
to a very small value. The effect of nitric oxide was found to be transient however, and a subsequent rise in rate occurred until after about 10 to 20% of the ethylene had reacted, when the rate became equal to the normal rate of polymerization.

It was concluded on this evidence that the nitric oxide was reacting with free radicals formed in the system, and was thereby breaking chain reactions. Burnham and Pease suggested that the transient effect of the nitric oxide was due to a state of equilibrium occurring between the free radicals and the nitric oxide,

$$R^- + NO \rightleftharpoons RNO.$$  \hspace{1cm} (19)

The work of Taylor and Bender (19) on the thermal decomposition of formaldoxime does not support this theory. They concluded that all the facts of nitric oxide inhibition, where methyl radicals are involved, can be explained on the assumption that a CH$_3$NO complex is initially formed, which isomerizes into formaldoxime. The formaldoxime then decomposes yielding cyanides, ammonia, etc. This theory is supported by the fact that cyanides and ammonia have been found among the products of nitric oxide inhibited reactions by a number of workers.

From the foregoing discussions it seems reasonable to conclude that methyl radicals formed by reactions such
as (10) and (17) play an important part in any free radical mechanisms which may be occurring. It is, therefore, difficult to explain the rise in polymerization rate observed by Burnham and Pease, which occurs when appreciable amounts of nitric oxide are present in the reacting system.

Molera and Stubbs (11) found that at 623°C, and an initial pressure of 210mm. of ethylene, nitric oxide caused a decrease in the rate of polymerization. They do not report any subsequent rise in the rate as was observed by Burnham and Pease (18). Molera and Stubbs observed that at 713°C, small amounts of nitric oxide reduced the polymerization rate without affecting the subsequent decomposition rate, but with larger amounts of nitric oxide the decomposition rate was seen to increase. This same acceleration in the rate of decomposition was observed at 773°C.

Molera and Stubbs postulated that the apparent inhibitory effect of the nitric oxide on the rate of polymerization was due to the reaction of the nitric oxide with radicals in the system, thereby breaking chains. It was suggested that the acceleration of the decomposition reactions was due to the oxidation of ethylene by nitric oxide.

The observed increase in the rate of decomposition
must make the actual effect of the nitric oxide on the polymerization rate uncertain. It would be expected that small amounts of nitric oxide would also give rise to the oxidation reactions which appear to occur when large amounts of nitric oxide are present. These reactions would lead to an apparent decrease in the rate of polymerization of ethylene, and hence it cannot be definitely concluded from the experimental evidence that the observed decrease in the rate of polymerization is entirely due to the reaction of the nitric oxide with free radicals.

Thus although it appears probable that free radical reactions are occurring in the thermal polymerization of ethylene, the results obtained from the investigation of the reaction in the presence of nitric oxide are inconclusive. Clearly, further work is needed on this problem.

(vi) Summary.

When heated at temperatures in the region of 300°C to 500°C, ethylene polymerizes to give higher mono-olefines. A small amount of decomposition also occurs at these temperatures.

At very high temperatures, decomposition reactions predominate. Thus at 1100°C and 1400°C, the principal products of pyrolysis are acetylene and hydrogen.
At intermediate temperatures both decomposition and polymerization reactions occur, and a variety of products are formed. These include propylene, butylene, butadiene, hydrogen, methane, and ethane.

The formation of methane indicates that free radical reactions are occurring in the system. It has been concluded that this compound is formed by decomposition of the higher olefines present among the products of pyrolysis. The results obtained from the investigation of the thermal decomposition of ethylene in the presence of nitric oxide also indicate the occurrence of free radical mechanisms. This evidence is inconclusive, however, since secondary reactions, such as the oxidation of ethylene by nitric oxide, appear to occur.
FIGURE 1: FLOW APPARATUS.
2. EXPERIMENTAL

(a) Outline of experimental method.

The ethylene used in the experiments was taken from a small cylinder of anaesthesia ethylene supplied by the British Oxygen Co. Ltd. Portions of this gas were purified in a flow system, and the purified gas was passed through a reaction vessel heated in an electric furnace. The condensible and non-condensible products of pyrolysis were collected in a series of traps, and were subsequently analysed by low temperature fractional distillation and gas analysis. The apparatus described below was subsequently used in a slightly modified form for the investigation of the thermal decomposition of tetrafluoroethylene.

(b) The flow apparatus for the thermal decomposition of ethylene.

(i) Apparatus.

The apparatus is illustrated in Figures 1 and 2. It was constructed entirely from soda glass, except for the oxygen absorption vessel J and the reaction vessel R, which were constructed of Pyrex glass and silica respectively. These vessels were joined to the soda glass apparatus by means of standard taper joints sealed with picein. All taps were hollow-key vacuum taps, and these were lubricated with Apiezon M grease.
The wash-bottles A and B contained strong sodium hydroxide solution and water respectively, to remove any acid gases present in the ethylene. The mercury valve C was included between the wash-bottle B and the flowmeter D to prevent any build up in pressure, should a blockage occur in any part of the flow system.

The flowmeter D was constructed to measure rates of flow up to 10 litres per hour, to within an accuracy of ± 0.5 litre. It consisted of a 6cm. length of 0.5mm. bore capillary tubing and a U-tube containing water. The two arms of the U-tube were joined to the tubing at either end of the length of capillary as shown.

Any oxygen present in the ethylene was removed using the method described by Meyer and Ronge (26). The oxygen absorption vessel J consisted of a Pyrex tube 50cm. in length and 3cm. in diameter, and a small bulb 4cm. in diameter joined to the bottom of the tube. Taps E and F were joined to this bulb as shown. The vessel contained activated copper prepared as described below. A heating coil of 28 S.W.G. nichrome wire of 90 ohms resistance was wound on the outside of the tube. The coil was connected to the 230 volt a.c. mains in series with a rheostat. A tube 5.5cm. in diameter placed over the coil and secured at the top and bottom by
FIGURE 2:

PUMPING SYSTEM
means of asbestos string, served as a jacket to prevent loss of heat. The drying tube K, 60 cm. long and 2 cm. in diameter, was packed with calcium chloride, and the tube L of similar size was packed with a mixture of phosphorus pentoxide and glass beads.

The reaction vessel H consisted of a silica tube 25 cm. in length and 2.2 cm. internal diameter, having capillary inlet and outlet tubes at either end, each 30 cm. in length, to allow rapid heating and cooling of the gas. The vessel was fitted with a thermocouple well extending along its axis from the inlet end to a point 2 cm. from the outlet end of the vessel. The pressure at either end of the reaction vessel could be measured on the manometers M and N. The outlet end of the reaction vessel was connected through tap X to the pump, and through taps T, U, and V, to the collecting traps 1, 2, and 3, as indicated.

The traps 1 and 2 of 140 and 60 ml. capacity respectively, were connected through taps W and 0 to the pump, and through taps W and Y to the low temperature fractional distillation column. The 60 ml. capacity charcoal trap 3 was connected through tap Z to the Toepler pump and gas analysis apparatus. Each of the three traps was fitted with a manometer.

A mercury-vapour pump C (Figure 2) backed by a rotary oil pump was used to evacuate the apparatus up to tap H, to a pressure of $10^{-5}$ mm. of mercury or less.
Trap A (Figure 2) was cooled in liquid nitrogen when the pumps were in use. A tilting McLeod gauge attached at B by means of a standard joint, was used to determine the pressure in the evacuated portion of the apparatus.

(ii) The activated copper compound.

The activated copper for the absorption of oxygen was prepared by the method described by Meyer and Ronge(26). 120g. of basic copper carbonate were dissolved in 2 litres of ammonia, and 420g. of kieselguhr were added to the solution. The mixture was then evaporated to dryness on the steam bath. The solid cake obtained was broken into small lumps, which were then heated in an oven at approximately 170°C. until they had a brownish colour. The material was freed from dust by sifting, and packed into the absorption vessel. The heating coil was switched on, and the rheostat adjusted to give a temperature of 200°C. inside the absorption vessel. A stream of hydrogen was then passed through the reaction vessel, entering at the top, and leaving through tap S. The copper oxide was thereby reduced, and finally the material in the absorption vessel changed to a dark violet colour.

The heating coil was switched off and tap E was opened for a short while to allow the water that had
collected in the small bulb to drain off. When the tube had cooled to room temperature, the flow of hydrogen was stopped, tap S was closed, and the absorption vessel was fitted into the apparatus as shown.

(iii) Calibration of the flowmeter.

Before carrying out the experiments described below, the flowmeter D (Figure 1) was calibrated by passing a steady stream of ethylene through the flow apparatus and collecting the gas in traps 1, 2, and 3. The procedure adopted was similar to that described below, except that the furnace and oxygen absorption vessel were at room temperature. The difference in height of the liquid in the two arms of the flowmeter U-tube was noted and the volume of gas collected in a known time was measured. The operation was repeated at different flow rates, and a graph of rate of flow against height of liquid in the flowmeter U-tube was plotted from the results obtained.

(iv) Preparation of the flow apparatus.

Trap 3 was half filled with animal charcoal. A small electric heater was placed around the trap and the charcoal was outgassed by heating in vacuo at 300°C for approximately 24 hours.

The furnace was switched on, and the furnace
control was adjusted to give the required temperature. The oxygen absorption vessel was heated to 200°C, and all sections of the apparatus, except the portion between the tap H and the cylinder of ethylene, were evacuated to a pressure of $10^{-5}$ mm. or less.

The traps 1, 2, and 3, were cooled in liquid nitrogen, and the apparatus was then ready for use.

(v) Procedure for operation of the flow apparatus.

A steady stream of gas from the cylinder was passed for a few minutes through the wash bottles and flowmeter and out through the tap G and mercury valve F (Figure 1) to displace the air from this section of the apparatus. Tap G was then closed, and H was slowly opened to admit the gas from the cylinder to the section of the apparatus up to taps T and X. When the manometers M and N indicated that a pressure of 1 atmosphere had been reached in this section of the apparatus, tap P was opened for a few minutes to allow the gases which had remained in the reaction vessel during filling, to pass out of the apparatus through the mercury valve q. The cylinder valve was then adjusted to give the required rate of flow of ethylene through the apparatus, as shown by the height of the liquid in the flowmeter U-tube.
Tap P was closed, and T was slowly opened to allow the products of pyrolysis to pass into the collecting traps. The time was noted, and the tap T and the cylinder valve were adjusted to give a pressure of one atmosphere inside the reaction vessel with the required rate of flow. The condensible products of pyrolysis were collected in traps 1 and 2, and the non-condensible products were absorbed in the activated charcoal in trap 3. Frequent adjustment of the cylinder valve and tap T were necessary during a run to maintain the required rate of flow and a pressure of 1 atmosphere in the reaction vessel.

When the required amount of gas had been passed through the reaction vessel, taps T, U, V, and H, were closed and G was opened. The cylinder valve was then closed, and the gas in the apparatus between taps H and T was removed by pumping.

The condensible products of pyrolysis were subsequently transferred to the low temperature distillation column, and analysed by fractional distillation. On warming the charcoal trap 3, the non-condensible products of pyrolysis were evolved. They were transferred to a measuring burette by means of a Toepler pump, and analysed in an Orzat type gas analysis apparatus.
(c) The electric furnace, and the distillation apparatus.

The reaction vessel R (Figure 1) was heated in a wire wound, horizontal, tubular type furnace. The same furnace was used in the investigation of the thermal decomposition of tetrafluoroethylene by the flow method. The temperature inside the reaction vessel was measured using a chromel-alumel thermocouple in conjunction with a Doran potentiometer. A full description of the furnace and the method of temperature measurement are given in Section (c) of Part II of this thesis.

The condensable products of pyrolysis were analysed using a low temperature fractional distillation column of the Podbielniak type. A description of the distillation apparatus, and the method of operation are given in Section (d) of Part II. The larger of the two columns was used for the analysis of the products of pyrolysis of ethylene.

(d) The gas analysis apparatus for the examination of the non-condensable products of pyrolysis of ethylene.

(i) Introduction.

The non-condensable products of pyrolysis of ethylene as taken from the charcoal trap, were found to consist of a mixture of nitrogen, methane, and hydrogen. By carrying out a series of blank runs in which the furnace was kept at room temperature, it was found that the ethylene
FIGURE 3:
GAS ANALYSIS APPARATUS
from the cylinder contained a small fixed amount of nitrogen. The methane and hydrogen were true products of pyrolysis. It was, therefore, only necessary to analyse the mixture for methane or hydrogen, since the amount of nitrogen present could be derived using the figures obtained from the blank runs, and the amount of remaining gas could be calculated by difference. The gas analysis apparatus was constructed for the measurement of the total volume of non-condensible products, and the determination of the amount of hydrogen present in the mixture. The apparatus and method used were similar to those described by Brooks, Lykken, et al. (27).

(ii) Apparatus.

The apparatus used is illustrated in Figure 3. It was constructed entirely of soda glass, except for the Pyrex U-tube G. Taps 1, 2, 10, and 11, were hollow key vacuum taps; 3 and 4 were hollow-key, double-oblique vacuum taps; 5, 6, 7, and 8, were solid-key, 1mm. T-bore capillary taps; 9 was also a solid key capillary tap. All taps and joints were lubricated with Apiezon M grease.

The vessel A of approximately 320ml. capacity was connected through the tap 10 to a mercury reservoir B, by means of pressure tubing. The 50ml. burette C was surrounded by a water jacket to prevent temperature fluctuations, a mercury thermometer gave the temperature of the water in
the jacket. The graduated volume of the burette included all the space up to the barrel of the tap. The burette was connected through tap 11 to the mercury reservoir D by means of thick walled rubber tubing.

The U-tube G, which was connected to taps 5 and 6 by means of tapered joints, was constructed of 6mm. bore Pyrex tubing, the length of each arm being 20cm. The U-tube was heated by means of a small coil of 30 S.W.G. nichrome wire, wound onto a Pyrex boiling tube 21cm. long and 4cm. in diameter. The coil was connected to the a.c. mains in series with a variable resistance. A copper-constantan thermocouple in conjunction with a Doran potentiometer, was used to measure the temperature in the boiling tube.

The vessel E of approximately 60ml. capacity, was connected to the mercury reservoir F by means of thick walled rubber tubing. One limb of the U-shaped absorption vessel J was connected to the tap 8 by means of a tapered joint, the other limb was open. The volume of each limb was approximately 80ml. The closed limb was packed with lengths of 3mm. bore, thin walled glass tubing, in order to increase the surface area of the absorbing reagent. The other limb served as a reservoir for the reagent.

(iii) Reagents.

Copper oxide wire (for the determination of hydrogen).
The micro-analytical reagent supplied by Hopkin and Williams Ltd. was used.

**Pyrogallol solution** (for oxygen absorption). 100ml. of a 50% solution of potassium hydroxide were placed in a conical flask, and a stream of nitrogen was bubbled into the solution to remove oxygen from the flask. 15 g. of pyrogallol were then added in small portions, the nitrogen being bubbled continuously into the solution.

(iv) **Preparation of the apparatus.**

A stream of nitrogen was blown through the absorption vessel J, to expel atmospheric oxygen. The pyrogallol solution was then poured into the vessel until both limbs were a little more than half full. A little liquid paraffin was poured into the open limb to prevent the surface of the pyrogallol solution from coming into contact with the air. The absorption vessel was then connected to the apparatus and the level of the liquid in the closed limb was drawn up to a point just below tap 8. This tap was then closed. The level of the mercury in vessel E was raised to a point just below tap 7, and this tap was closed.

The U-tube G was filled with copper wire, and this was heated to 270°C, the temperature being controlled to ±10°C, by means of the rheostat.

The apparatus was tested for leaks in the following
manner. Approximately 50ml. of air were drawn into the burette, tap 9 was closed, and tap 5 was turned so that the tubing between taps 4 and 9 and also the U-tube G were connected with the burette. This section of the apparatus was then placed under pressure by raising the reservoir D. The mercury level in the burette was noted, and the apparatus was allowed to stand for 10 to 15 minutes. The height of the mercury in the burette was then checked, and the levels of the mercury in E and of the reagent in J were also noted. The fact that none of these levels had changed indicated that the apparatus was free from leaks.

The sample of air was passed into the absorption vessel J, it was allowed to remain in the absorption vessel for 10 seconds, and was then withdrawn to the burette. This process was repeated until a constant residual volume was obtained, indicating that all the oxygen had been removed from the sample of air. The residual gas was used to sweep out the air in the U-tube G and in the connecting tubes between taps 4 and 9, thereby removing all oxygen from the apparatus.

Taps 3 and 4 were turned to connect A with G, and the reservoir D was raised to fill the burette and the tubing between 3 and 4 with mercury. Taps 3 and 4 were closed and the reservoir B was lowered until the mercury level in A
was just above the barrel of tap 10. This tap was then closed, and A was evacuated by pumping. Tap 1 was closed, and the apparatus was ready for use.

(v) **Procedure for operation of the apparatus.**

A portion of the non-condensible gases was transferred from the charcoal trap to the vessel A. Approximately 20ml. of the gaseous mixture were transferred from A to the burette B, the exact volume of gas in the burette was noted, and also the temperature in the water jacket and the barometric pressure.

The sample of gas in the burette was passed through the U-tube C into the mercury vessel E, by slowly raising the reservoir D and at the same time lowering F. It was then drawn back into the burette via the U-tube C by the reverse operation. This process was repeated until a constant residual volume was obtained, the total decrease in volume being equal to the volume of hydrogen present in the original sample. The residual gases were expelled from the apparatus.

A fresh sample of approximately 50ml. of the gaseous mixture was transferred from A into the burette. The volume of this sample was measured accurately and it was then expelled into the atmosphere. This process was repeated until all the gaseous mixture in A had been transferred to the burette and measured. A further sample was transferred from
the charcoal trap to A, and the total volume of this sample was determined as before.

The process of drawing the gases from the charcoal trap into A and subsequently measuring their volume by transferring them in portions into the burette, was repeated until only a trace of the gases remained in the charcoal trap. This residual volume was neglected.

From the results obtained, the total volume of the non-condensible gases at 0°C. and 760mm. pressure was calculated, and also the amount of hydrogen present in the mixture. The amount of nitrogen in the non-condensible gases was derived using the results obtained from the blank runs, and the methane was calculated by difference.
3. RESULTS.

(a) The examination of the gases present in the cylinder of ethylene.

A series of blank runs were carried out with the furnace at room temperature, to check the purity of the ethylene taken from the cylinder. The samples of condensible gas collected in each run were combined, giving a total volume of 8.4 litres of gas. This was distilled in the low temperature fractionating column, and found to be pure ethylene. The non-condensible gas samples were also combined giving a total volume of 80 ml. of gas.

The molecular weight of the non-condensible gas was determined by the vapour density method, and found to be 27.1 ± 1.0. No change in volume occurred when a sample of the gas was treated with acid cuprous chloride solution, and it was therefore concluded to be free from carbon monoxide. The gas was free from oxygen as it had passed through the tube packed with activated copper. It was therefore concluded that the non-condensible gas was nitrogen, together with a possible small percentage of methane. Since the volume of non-condensible gas present in the ethylene amounted to less than 1% of the total volume of gas, the trace of methane that it might contain was disregarded.
Figure 4.

Distillation of products of pyrolysis of ethylene at 650°C. (Run 4.)

Figure 5.

Distillation of products of pyrolysis of ethylene at 650°C. (Run 5.)
(b) The products of pyrolysis of ethylene.

A series of five runs were carried out in which ethylene was pyrolysed at 650°C and 1 atmosphere pressure. The yields of condensible products from the first three runs were insufficient to allow a complete analysis of the mixtures in the low temperature fractionating column. In runs 4 and 5 larger yields of products were obtained by increasing the amount of gas pyrolysed and decreasing the rate of flow of gas through the system.

RUN 4. A total volume of 13 litres of ethylene was passed through the flow apparatus at a rate of 3.0 litres per hour. The graph of the results obtained by the fractional distillation of the condensible products of pyrolysis is shown in figure 4. The gaseous distillate was collected in a 3.6 litre bulb.

The undistilled residue was transferred to trap 2 (Figure 1) and analysed by fractionation between traps 1 and 2. The results obtained from this fractionation are given in Table 1. The identity of the various fractions was ascertained by comparison of the vapour pressure figures obtained with those given in the Table compiled by Stull (28).

The non-condensible gas was analysed for hydrogen in the gas analysis apparatus. The nitrogen present was equal to 1% of the total volume of ethylene passed through
the flow apparatus. The remainder of the non-condensible
gas was taken as methane.

Table 1.

Separation of the materials retained in the column.

<table>
<thead>
<tr>
<th>Material Retained</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residue cooled to -105°C</td>
<td>Distilled to trap cooled to -196°C, ~100 ml. of gas with vapour pressure corresponding to ETHYLENE.</td>
</tr>
<tr>
<td>Portion retained at -105°C cooled to -85°C</td>
<td>Distilled to trap cooled to -196°C, ~65 ml. of gas with vapour pressure corresponding to 1,3-BUTADIENE.</td>
</tr>
<tr>
<td>Portion retained at -85°C cooled to -60°C</td>
<td>Distilled to trap cooled to -196°C, ~75 ml. of gas with vapour pressure corresponding to C5 HYDROCARBONS.</td>
</tr>
<tr>
<td>Portion retained at -60°C cooled to -48°C</td>
<td>Distilled to trap cooled to -196°C, ~90 ml. of gas with vapour pressure corresponding to C6 HYDROCARBONS.</td>
</tr>
</tbody>
</table>

0.164 g. of material retained at -48°C with vapour pressure corresponding to C7 HYDROCARBONS and above.
The complete analysis of the products of pyrolysis obtained in Run 4 is shown in Table 2.

From the rate of flow of the gas through the reaction vessel, the reaction time was calculated to be 25 seconds.

Table 2.

The products of pyrolysis of ethylene at 650°C. (Run 4).

G. mol. per 100 g. mol. of ethylene passed:

<table>
<thead>
<tr>
<th>Product</th>
<th>G. mol. per 100 g. mol. of ethylene passed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>0.94</td>
</tr>
<tr>
<td>Methane</td>
<td>1.85</td>
</tr>
<tr>
<td>Ethylene</td>
<td>85.45</td>
</tr>
<tr>
<td>Ethane</td>
<td>2.27</td>
</tr>
<tr>
<td>Propylene</td>
<td>2.49</td>
</tr>
<tr>
<td>C4 Hydrocarbons</td>
<td>1.57 (approx 30% butadiene)</td>
</tr>
<tr>
<td>C5 Hydrocarbons</td>
<td>0.57</td>
</tr>
<tr>
<td>C6 Hydrocarbons</td>
<td>0.68</td>
</tr>
<tr>
<td>C7 Hydrocarbons and above</td>
<td>approx 0.010 g. per g. of ethylene passed</td>
</tr>
</tbody>
</table>

Total volume of ethylene passed..... 13 litres
Percentage decomposition......... 14.54 %

**RUN 5.** A total volume of 12 litres of ethylene was passed through the flow apparatus at a rate of 2.6 litres per hour. The graph of the results obtained by the fractional distillation of the products of pyrolysis is shown in Figure 5. The gaseous distillate was collected in a 3.6 litre bulb. A small amount of liquid remaining in
the column after the butene fraction had been distilled off, was analysed by further fractionation in the column, at a reduced pressure. The fractions separated by the distillation at reduced pressure were identified by comparison with the vapour pressure figures given by Stull (26). The non-condensible products were analysed as before.

The complete analysis of the products of pyrolysis obtained in Run 5 is shown in Table 3.

The reaction time was calculated to be 26 seconds.

Table 3.
The products of pyrolysis of ethylene at 650°C. (Run 6).

<table>
<thead>
<tr>
<th>G. mol. per 100 g. mol. of ethylene passed.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen.................................. 0.91</td>
</tr>
<tr>
<td>Methane................................... 1.74</td>
</tr>
<tr>
<td>Ethylene.................................. 85.39</td>
</tr>
<tr>
<td>Ethane.................................... 2.22</td>
</tr>
<tr>
<td>Propylene.................................. 2.68</td>
</tr>
<tr>
<td>C4 Hydrocarbons.......................... 1.70 (approx 30% butadiene)</td>
</tr>
<tr>
<td>C5 Hydrocarbons.......................... 0.83</td>
</tr>
<tr>
<td>C6 Hydrocarbons and above............ approx 0.02 lg. per g. of ethylene passed.</td>
</tr>
</tbody>
</table>

Total volume of ethylene passed...... 12 litres
Percentage decomposition.............. 14.64 %

Small amounts of carbon were deposited on the walls of the reaction vessel during these runs. The liquid products
obtained were yellow in colour, and were therefore concluded to contain highly unsaturated compounds.

It was not possible to assess the exact amount of liquid products formed in the runs carried out at 650°C, as small quantities of an oily liquid product were seen to collect in the connecting tubing between the reaction vessel and trap 1 (Figure 1) during the pyrolysis. The weights of these small amounts of liquid are not included in Tables 2 and 3.
4. **DISCUSSION**

The results given above show that the products obtained from the pyrolysis of ethylene at 650°C. were similar to those found by other workers who investigated the thermal decomposition of ethylene at 1 atmosphere pressure in this temperature region.

On the basis of this observation it was concluded that the experimental technique employed in the above investigation was quite satisfactory, and hence that the main purpose of the work had been achieved. It is not possible to make a quantitative comparison with previous results, as the reaction time was different from those employed by other workers.

The experimental results are of little use as regards the elucidation of reaction mechanisms. The various products formed can be accounted for equally well on the basis of the free radical mechanism proposed (see page 13), and also on the basis of the mechanisms postulated by Burke, Baldwin, and Whitacre (8).

From the work of Pease (10) it is seen that at low temperatures and high pressures, ethylene polymerizes to give high molecular weight olefines. The polymerization process is accompanied by decomposition of the products
FIGURE 6.

GRAPH OF $\log_{10} k$ AGAINST $\frac{1}{T}$.

- EXPERIMENTAL RESULTS.
- RESULTS OF PEASE.
and of the ethylene itself. The amount of decomposition occurring increases with increase in the temperature of the reacting gas.

Under the experimental conditions employed by Pease the amount of decomposition occurring was very slight compared with the amount of polymerization taking place. Pease calculated a series of values for the velocity constant, $k$, of the initial reaction in the polymerization process, which he expressed as the fraction of ethylene which would react in one hour if the pressure of that gas were maintained constant at 1 atmosphere, and the reaction were actually second order.

A graph of $\log_{10} k$ against $\frac{1}{T}$ plotted from the figures given by Pease(10) is shown in Figure 6. The divergence between the values for $k$ at a particular temperature is seen to increase with temperature. This increase in divergence is to be expected since the error arising from the neglect of the decomposition reactions will increase with temperature. Thus two values of $k$ obtained for two different reaction times at $350^\circ C$, will differ less than the two values of $k$ obtained for the same two reaction times at $500^\circ C$, assuming that the initial ethylene pressures are the same in all cases.
Values of 24.6 and 24.1 atm\(^{-1}\)hr\(^{-1}\) were obtained for \(k\) at 650\(^0\)C. from the results given in Tables 2 and 3. These values were calculated using the same assumptions as those made by Pease (10). It is seen from Figure 6 that the two experimental values lie just below the line drawn through the lower limits of the values obtained by Pease. This is probably due to the fact that the amount of decomposition products formed, such as hydrogen and methane, was greater than the amount formed in the experiments carried out by Pease. The proximity of the two values of \(k\) to the lower limit obtained by extrapolation of the results of Pease indicates that at 650\(^0\)C. the main primary reaction occurring is the same as that taking place at 500\(^0\)C. This postulate is confirmed by the work of Molera and Stubbs (11) who obtained the same value for the energy of activation of the primary reaction occurring over the temperature range 623\(^0\) to 713\(^0\)C., as was obtained by Pease for the primary reaction occurring over the temperature range 250\(^0\) to 500\(^0\)C.
PART II: THE THERMAL REACTIONS OF TETRAFLUOROETHYLENE.

1. THE PREPARATION AND PROPERTIES OF THE SIMPLER FLUOROCARBONS.

(a) Saturated fluorocarbons.

(i) Preparation.

Saturated fluorocarbons can be prepared by the catalysed reaction between carbon and fluorine. It was found by Ruff and Keim (29) that carbon tetrafluoride was one of the products formed from the high temperature reaction between carbon and fluorine. This procedure could not be used as a general method of preparing the fluorocarbon however, as violent explosions frequently occurred when fluorine was brought into contact with carbon. Simons and Block (30) found that mercury and its compounds were good catalysts for the reaction between carbon and fluorine. The catalysts enabled the reaction to proceed smoothly without explosions, giving rise to the formation of carbon tetrafluoride and significant proportions of higher boiling fluorocarbons such as C₂F₆, C₃F₈, and C₄F₁₀. Other efficient catalysts for this reaction were soon discovered (31).

It was found by Bigelow et al. (32) that when a mixture of ethane and fluorine were passed through a brass tube filled with fine mesh copper gauze, carbon tetrafluoride and hexafluoroethane were produced together with various
partly fluorinated derivatives of methane and ethane. This method, which is known as the catalytic fluorination process, has been developed by Cady, Grosse, et al. (33). It was found, however, that the method could not be satisfactorily extended to large scale production since the precise control of temperature and other variables was difficult. The method has therefore been superseded by the metallic fluoride process.

The metallic fluoride method of preparing fluorocarbons from hydrocarbons followed from the discovery of the method of preparation of cobaltic fluoride from cobaltous fluoride and fluorine by Ruff (34), and Ruff and Ascher (35). This compound was found to be a powerful fluorinating agent. It was used by Ruff and Keim (36) to replace chlorine by fluorine in carbon tetrachloride. The method of preparing fluorocarbons from hydrocarbons using cobalt fluoride was developed by Fowler et al. (37). The process is carried out in two steps. Firstly cobaltous fluoride is converted into cobaltic fluoride by the action of fluorine. The hydrocarbon to be fluorinated is then passed in the vapour phase over the trifluoride. The cobaltic fluoride is reduced to cobaltous fluoride during the reaction, and it is then reoxidised back to the cobaltic state.
The need for a general method of preparing fluorocarbons which did not involve the use of elementary fluorine, led to the discovery by Simons et al. (38) of a direct electrochemical process which produced fluorocarbons directly in one step, without the employment or generation of any elementary fluorine. In this process the hydrogen in an organic compound is replaced by fluorine. The organic chemicals are dissolved in liquid hydrogen fluoride, or are in contact with liquid hydrogen fluoride made conducting with some electrolyte. The process is carried out at potentials considerably below that necessary to generate fluorine. Hydrogen is generated simultaneously with the fluorocarbon, but as there is no reaction between these two products under the conditions of operation of the cell, separate compartments are not necessary. Thus the cell designs are very compact.

Many organic compounds, particularly those containing oxygen, nitrogen, or sulphur, are not only soluble in liquid hydrogen fluoride, but the solutions are highly conducting. Passage of an electric current through these solutions with suitable electrodes and at low potentials results in the production of fluorocarbons or fluorocarbon derivatives or both. Some organic compounds such as hydrocarbons are only very slightly soluble in hydrogen fluoride.
or do not form electrically conducting solutions. These substances can, however, be used in the electrolytic process by simply adding some material, either organic or inorganic, which will provide conductivity.

Carbon tetrafluoride is formed in good yield by the electrolysis of solutions of acetic acid, acetyl chloride, acetonitrile, acetone, methanol, and ethanol, in liquid hydrogen fluoride (38). Hexafluoroethane is obtained by the electrolysis of solutions of trifluoroacetic acid (39), and propionic acid (38), in liquid hydrogen fluoride.

(ii) Properties.

Carbon tetrafluoride: The following physical properties are generally accepted as being the most accurate,

melting point, $-184^\circ C$.

boiling point, $-128^\circ C$.  

vapour pressure of the liquid over the range $-180.6^\circ C$ to $-127.3^\circ C$,

$$\log_{10} p_{\text{mm}} = 5.04420 - 701.73/T + 1.75 \log_{10} T - 0.0076715 T.$$

(latent heat of vaporization, 2.947 k.cal. per mole.

Trouton's constant, 20.3.  

Carbon tetrafluoride is by far the most inert of the fluorocarbons. It has been found to react only slightly even at the temperature of a carbon arc to give low yields
of tetrafluoroethylene and hexafluoroethane (42).

The reactions of carbon tetrafluoride with a number
of inorganic substances were reported by Ruff and Keim (29). They found that sodium, magnesium, and barium burn in the gas at high temperatures. The gas was found to be inert to most other metals and non-metals. Simons and Block (30) found that carbon tetrafluoride reacted with alkali metals at about 400°C, giving the metal fluoride and carbon. Higher molecular weight fluorocarbons were found to react in a similar manner, and this reaction has been used as a basis for methods of fluorocarbon analysis.

Like most other fluorocarbons, carbon tetrafluoride is not attacked by oxidising agents such as nitric acid, fuming sulphuric acid, nitrating mixture, acid chromate or permanganate at ordinary temperatures. Fluorocarbons are not readily attacked by the usual aqueous reducing agents, nor by acids or aqueous alkali.

Hexafluoroethane:— The following physical properties were reported by Ruff and Bretschneider (42),

melting point, -100.6°C.

boiling point, -78.2°C.

vapour pressure of the liquid over the range -99.3°C.

to -77.5°C.

\[ \log_{10} P_{mm} = 7.376 - 875.7/T. \]
latent heat of vaporization, 4064.6 cal. per mole.

Trouton's constant, 20.5.

Pace and Aston (43) determined the vapour pressure of solid and liquid hexafluoroethylene and obtained the following relationships,

LIQUID: \( \log_{10} p_{\text{mm}} = 14.225677 - 1125.3291/T - 2.33917 \log_{10} T - 0.00109858T \)

SOLID: \( \log_{10} p_{\text{mm}} = 24.307 - 2227/T - 0.0915 \log_{10} T - 0.05161T \)

melting point, -100.1°C.

boiling point, -78.29°C.

latent heat of vaporization, 3859.5 cal. per mole.

These results differ somewhat from those of Ruff and Bretschneider (42). On plotting a graph of \( \log_{10} p_{\text{mm}} \) against \( 1/T \) (see Figure 24) the results of Pace and Aston are seen to give two curves which cross in such a way that the vapour pressure of the metastable state is less than that of the stable state. As this condition cannot occur in practice, the results of Pace and Aston must be incorrect.

Starting with hexafluoroethane there is a gradual increase in the reactivity of acyclic fluorocarbons as the number of carbon atoms in the molecule increases. Hexafluoroethylene is much more reactive than carbon tetrafluoride,
due partly to the fact that it contains the relatively weaker carbon-carbon bond. Brice, Pearlson and Simons (44) found that on heating a mixture of hexafluoroethane and chlorine to 937°C to 944°C, the gases reacted to give chlorotrifluoromethane. The corresponding bromo derivative was obtained when hexafluoroethane and bromine were heated to 896°C to 912°C.

White and Rice (45) investigated the kinetics of the reaction of hexafluoroethane with quartz over the temperature range 800°C to 842°C. They found that a heterogeneous reaction occurred for which they suggested the following equation,

$$C_2F_6 + \frac{3}{2}SiO_2 \rightarrow CO + CO_2 + \frac{3}{2}SiF_4$$

The lowest temperature at which the above reaction occurred was found to be in the region of 600°C. It appeared that homogeneous decomposition of hexafluoroethane did not take place below 342°C.

(b) The perfluoro-olefins.

(i) Preparation.

The earliest reported member of this series was tetrafluoroethylene, and this is the only perfluoro-olefine which has been studied in any detail. Some of these compounds have been prepared by general methods analogous to those used for preparing hydrocarbon olefines, and various new
preparative procedures have also been developed.

One general method of preparation makes use of the fact that chlorine and bromine atoms may be removed from chlorofluoro- and bromofluoro- compounds by reduction with zinc in alcohol, or acetone. A similar method is used for preparing hydrocarbon olefines. The method based on the removal of hydrogen halide by means of alcoholic alkali can only be used when hydrogen atoms remain in the molecule after the removal of the hydrogen halide group.

Certain special methods for preparing individual fluoro-olefines are described below.

(ii) Physical properties.

Apart from the melting points and boiling points of the first three members of this series, few physical data are available. The low molecular weight fluoro-olefines have higher melting and boiling points than their hydrocarbon analogues, and whereas the hydrocarbon olefines of low molecular weight boil at lower temperatures than the corresponding saturated hydrocarbons, even tetrafluoroethylene boils at a slightly higher temperature than hexafluoroethane. The boiling points of fluoro-olefine isomers appear to differ in a reverse manner to that found with hydrocarbon olefines. Thus butene-1 boils at a lower temperature than butene-2,
whereas octafluorobutene-1 boils at a higher temperature than octafluorobutene-2.

(iii) **Chemical properties.**

A number of the reactions of the perfluoro-olefines are analogous to those of hydrocarbon olefines. Thus chlorine and bromine form addition products with perfluoro-olefines, and hydrogen fluoride, chloride, and bromide have been added to tetrafluoroethylene in the vapour phase.

The perfluoro-olefines are readily oxidised by potassium permanganate, and this reaction can be used as an approximately quantitative determination of unsaturation. The determination can be carried out by titration of a solution of the perfluoro-olefine in acetone with a dilute solution of potassium permanganate in acetone.

An interesting reaction found to occur with perfluoro-olefines is the addition of alcohols by the action of alcoholic solutions of the alkali alcoholates. This type of addition to an olefinic linkage has previously been found to occur only when an electron-attractive group such as carbonyl or nitrile is attached to the unsaturated carbon atom as in \(\alpha,\beta\)-unsaturated ketones, aldehydes, esters and nitriles.

In the absence of any accurate kinetic data it is difficult to compare the reactivities of hydrocarbon olefines
and perfluoro-olefines. A qualitative comparison between ethylene and tetrafluoroethylene can, however, be made from the available experimental data. This will be discussed later.

(iv) **Tetrafluoroethylene.**

**Preparation:** Tetrafluoroethylene was first prepared by Thornton, Burg, and Schlessinger (46) by the action of a high voltage discharge on dichlorodifluoromethane. It was prepared by Ruff and Bretschneider (42), together with hexafluoroethane, by passing carbon tetrafluoride to and from several times through a carbon arc.

Locke, Brode, and Henne (47) prepared dichlorotetrafluoroethylene by the action of antimony fluoride on hexachloroethane, and obtained tetrafluoroethylene by reduction of the product with zinc and alcohol.

Tetrafluoroethylene is synthesized commercially by passing monochlorodifluoromethane through an inert reaction vessel of carbon, silver, or platinum at 650°C or higher. The products formed contain 80 to 90% of tetrafluoroethylene (48). A series of compounds having the general formula H(CF₂)ₙCl is also obtained, together with small amounts of hexafluoropropene, octafluorocyclobutane and various other cyclic fluorocarbons. Monobromodifluoromethane reacts in a similar manner.
The products of pyrolysis are separated by a continuous process (49) in which hydrogen chloride and tetrafluoroethylene are removed simultaneously from the other products by fractional distillation under pressure. The monochlorodifluoromethane is distilled from the remaining mixture and pyrolysed again by recycling through the reaction vessel.

Physical properties:— The following figures, reported by Ruff and Bretschneider (42), are generally accepted as being the most accurate,

- Melting point, \(-142.5^\circ \pm 0.5^\circ C\).
- Boiling point, \(-76.3^\circ \pm 0.3^\circ C\).
- Vapour pressure of the liquid over the range \(-132.0^\circ C\) to \(-81.2^\circ C\).

\[ \log_{10} p_{\text{sat}} = 7.618 - 931.9/T. \]

- Latent heat of vaporization, 4262 cal. per mole.
- Trouton’s constant, 21.7.
- Density of the liquid, \(2.333 - 0.00414T\) g. per cc.

The stability of tetrafluoroethylene:— Pure tetrafluoroethylene is quite stable at ordinary temperatures. Liquid tetrafluoroethylene containing more than 20 parts per million of oxygen is unstable at room temperature, however, and polymerizes on standing (50). This polymerization reaction is exothermic, and the heat generated by it is likely to
initiate the disproportionation of tetrafluoroethylene to
carbon and carbon tetrafluoride, an exothermic reaction
which can proceed with considerable violence (50). There is,
therefore, a risk of appreciable polymerization or explosion
when tetrafluoroethylene containing oxygen as impurity is
Tetrafluoroethylene is, therefore, always mixed with a stabilizer before it is compressed. The function of the stabilizer appears to be
the removal of any oxygen present, thus preventing polymerization
from occurring. A stabilizer commonly used for this purpose
is 'terpene B', which consists of a mixture of dipentene
and terpinolene (51). A number of other substances which can
be used for this purpose are mentioned in the patent literature
(50)(52)(53).

The thermal reactions of tetrafluoroethylene:- The thermal
stability of tetrafluoroethylene has been studied by Harmon
(54). He found that when the gas was heated under pressure
at 200°C., dimerization occurred giving octafluorocyclobutane.
This compound was also the principal product obtained when
tetrafluoroethylene under pressure was passed through a
tube containing activated charcoal at 4200°C. to 4500°C. Higher
boiling liquids believed to be completely fluorinated
cycloparaffins such as decafluorocyclopentane and hexadeca-
fluorocyclooctane were also obtained.

Harmon found that when tetrafluoroethylene was passed
through a tube at 695° to 730° C., a mixture of octafluorocyclo-
butane and a compound boiling at -31° C. was obtained. He
concluded that this latter compound was hexafluorocyclopropane.
It has since been shown that this conclusion was incorrect
and that the compound was actually hexafluoropropene. The
evidence in support of this will be discussed later.

On passing tetrafluoroethylene over a platinum
filament heated to 1340° C. Harmon found that the compound
which he incorrectly assumed to be hexafluorocyclopropane
was the principal product obtained.

Hazeldine (55) found that when tetrafluoroethylene
was heated in a silica tube at 200° C. for ten hours,
octafluorocyclobutane was the main product formed. A small
amount of a compound presumed to be hexafluoropropene was
also obtained.

An account of the thermal decomposition of tetrafluoro-
ethylene has recently been published (5). In this investigation
which formed part of the wartime project for development of
atomic energy, the thermal reactions of tetrafluoroethylene
were studied at various temperatures ranging from 435° C. to
750° C., using a flow method. The reaction vessel consisted
of a nickel tube packed with graphite.

The only product obtained from the thermal decomposit-
ion of tetrafluoroethylene at 435° C. was octafluorocyclobutane.
At 550°C, most of the tetrafluoroethylene which passed through the reaction vessel dimerized to give octafluorocyclobutane, small amounts of hexafluoropropene were also obtained, but no other products were formed at this temperature.

At temperatures in the region of 650°C, practically all the tetrafluoroethylene passed reacted to give appreciable yields of octafluorocyclobutane and hexafluoropropene. Small amounts of octafluorobutene-1 and liquids boiling above 100°C. were also obtained in this temperature region together with an inert gas which was concluded to be largely carbon tetrafluoride and hexafluoroethane.

At 750°C, octafluorobutene-1 was the major product formed together with appreciable amounts of the inert gas concluded to contain carbon tetrafluoride and hexafluoroethane. No octafluorocyclobutane was obtained and there was a big decrease in the yield of hexafluoropropene compared with that obtained at temperatures in the region of 650°C. The yield of high boiling products at 750°C. was approximately twice that obtained at 650°C.

These results agree generally with those of Harmon (54) and Haszeldine (55). The large decrease in the amount of hexafluoropropene obtained at 750°C. compared with that formed at 650°C. however, suggests that hexafluoropropene
is unlikely to be the major product of decomposition at 1340°C, as reported by Harmon.

The above results indicate that the major reaction occurring at temperatures below 650°C, is the dimerization of tetrafluoroethylene to give octafluorocyclobutane. This reaction is clearly very fast at 550°C, as after a reaction time of 10 to 15 seconds very little unreacted tetrafluoroethylene is obtained. The behaviour of tetrafluoroethylene at low temperatures is thus very different from that of ethylene, where butylene and high molecular weight olefines are the principal products formed (10). The following reactions have been suggested as the possible primary steps in the low temperature polymerization of ethylene (see pages 6 and 13)

\[ 2\text{C}_2\text{H}_4 = \text{CH}_3\text{-CH}_2\text{-CH=CH}_2 \]  
\[ 2\text{C}_2\text{H}_4 = \text{CH}_3^- + -\text{C}_3\text{H}_5 \]  

It is seen that both reactions (1) and (2) involve a hydrogen atom transfer, whereas in the reaction

\[ 2\text{C}_2\text{F}_4 = \text{CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2 \]  

no fluorine atom transfers occur.

It seems probable, therefore, that whereas little energy is required to transfer a hydrogen atom from one carbon atom to another, a similar transfer of a fluorine atom requires a much larger amount of energy, and cannot take place to any appreciable extent at temperatures below 550°C.
The fact that small amounts of octafluorobutene-1 are formed at 650°C. indicates that fluorine atom transfers do in fact take place at this temperature. The amount of octafluorobutene-1 formed is seen to increase with temperature, and a corresponding decrease in the yield of octafluorocyclobutane occurs. Since the dimerization reaction is very fast at 550°C., it seems probable that octafluorocyclobutane is unstable at temperatures above 550°C. and that ring opening occurs.

It appears, therefore, that the reactions which occur with tetrafluoroethylene are quite different from those which take place under similar conditions with ethylene. Owing to the high energy apparently necessary for fluorine atom transfers, the cyclic dimer is formed at lower temperatures rather than unsaturated fluoro-olefines. It is noteworthy that whilst this dimerization occurs readily with tetrafluoroethylene, ethylene does not react to give the cyclic dimer under any conditions.

When a mixture of ethylene and tetrafluoroethylene is heated at 150°C. and an initial pressure of 45 atmospheres, the gases react to give 1:1:2:2:2-tetrafluorocyclobutane (56) This suggests that the fluorine atoms attached to the carbon atoms in the cyclic compound impart a stability to
the ring, since a cyclic hydrocarbon is not formed under these conditions.

The photosensitized reactions of tetrafluoroethylene.- The mercury photosensitized reaction of tetrafluoroethylene has been studied (1), and the behaviour of this compound has been found to be quite different from that of ethylene.

From the work of Steacie (20) it seems probable that the primary step (4) in the mercury photosensitized reaction of ethylene

$$C_2H_4 + \text{Hg}^{(3P_1)} = C_2H_4^* + \text{Hg}^{('S_0') \text{ (4)}}$$

is followed by the following three reactions,

$$C_2H_4^* + C_2H_4 = 2C_2H_4 \quad (5)$$
$$C_2H_4^* = C_2H_2 + H_2 \quad (6)$$
$$C_2H_4^* = C_2H_3 + H \quad (7)$$

In the case of tetrafluoroethylene, however, the primary reaction

$$C_2F_4 + \text{Hg}^{(3P_1)} = C_2F_4^* + \text{Hg}^{('S_0') \text{ (8)}}$$

is followed by the reaction

$$C_2F_4^* = 2CF_2 \quad (9)$$

The difference between the reactions of the two compounds with excited mercury atoms is considered to be due to two factors;

(a) The difluoromethylene radicals formed in reaction
(g) are probably in the triplet state. In this state, the
two $p^w$ orbitals of the carbon atom will overlap with the
two $p^w$ orbitals of each fluorine atom. This overlap, which
does not occur with methylene, will tend to stabilize the
triplet state of the difluoromethylen radical.

(b) Owing to the high energy of the C-F bond and the
low energy of the F-F bond, as compared with the C-H and
H-H bond energies, reactions such as (6) and (7) will have
a very high heat of reaction in the case of tetrafluoroethylene,
and are therefore most unlikely to occur.

Addition reactions of tetrafluoroethylene:— Many of the
reactions of tetrafluoroethylene are analogous to those of
ethylene. Thus the gas reacts with bromine water to form
the dibromide (42), and with chlorine to form dichloro-
tetrafluoroethylene (57). Iodine in aqueous potassium
iodide solution does not react with tetrafluoroethylene (42)
but addition of iodine occurs to give diiodotetrafluoroethylene
at elevated pressures (58). The reaction between bromine
and tetrafluoroethylene appears to be heterogeneous, and it
has been found that unless a very strong bromine solution
is used, the addition reaction is slow and not quantitative (1).

The addition of hydrogen halides does not occur so
readily as in the case of ethylene. Thus, although addition
of hydrogen fluoride to ethylene occurs readily at room temperature and 10 atmospheres pressure (59), the corresponding addition to tetrafluoroethylene does not appear to take place under similar conditions (60). Addition of hydrogen fluoride to tetrafluoroethylene will occur, however, in the presence of a catalyst such as boron trifluoride (60).

The addition of hydrogen chloride and bromide to tetrafluoroethylene take place at about 300°C. in the presence of activated carbon (61), and hydrogen bromide addition occurs at 90°C. in the presence of a carbon-calcium sulphate catalyst (62). Unlike ethylene, tetrafluoroethylene appears to be unreactive towards metal salts such as mercuric sulphate(1).

A number of addition reactions occur with tetrafluoroethylene which have no parallel in the chemistry of ethylene. Thus, at 120°C. and 320 to 350 lb. per sq.in. pressure, sodium sulphite solution reacts with tetrafluoroethylene to give the addition compound \( \text{CF}_2\text{H} - \text{CF}_2\text{SO}_3\text{Na} \) (63). The addition of alcohols to perfluoro-olefines by the action of alcoholic solutions of the alkali alcoholates (64) has already been mentioned (see page 50). Tetrafluoroethylene reacts with a solution of sodium methoxide in methanol at room temperature and 20 atmospheres pressure to give the compound
The reaction between tetrafluoroethylene and primary and secondary aliphatic amines in the presence of water, is even more unusual. It was found that on heating a mixture of tetrafluoroethylene, diethyl ether, borax and butylamine at 100°C, for 8 hours under pressure, an appreciable yield of N-butyldifluoroacetamide was obtained (66). In this reaction, which may be represented by equation (10), the borax served as a source of water and also as a catalyst.

\[ C_2F_4 + BuNH_2 + 2OH^- = CF_2H-COONHBu + 2F^- + H_2O \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (10) \]

This reaction appears to involve a mechanism not hitherto encountered, since it entails the splitting of two C-F bonds, a process requiring a large amount of energy.

The following general conclusions can be made on the basis of the above experimental observations,

(a) Tetrafluoroethylene shows a decrease in reactivity towards electrophilic reagents such as bromine and hydrogen fluoride, as compared with ethylene.

(b) Tetrafluoroethylene shows a tendency to react with nucleophilic reagents such as alcohols and sodium sulphite.

This type of behaviour has been observed in compounds such as α3-unsaturated ketones, aldehydes, esters, and nitriles.
In these compounds the olefinic linkage exhibits a capacity for addition of nucleophilic reagents and a decreased reactivity towards electrophilic reagents. This behaviour has been attributed to the electron attractive tendencies of the \(-\text{C} = \text{O}\) and \(-\text{C} = \text{N}\) groups which give rise to the following electromeric changes,

\[
\begin{align*}
\text{C} &= \text{C} - \text{C} = \text{O} \quad \Rightarrow \quad \text{C} - \text{C} = \text{C} - \text{O} \\
\text{and} \quad \text{C} &= \text{C} - \text{C} \equiv \text{N} \quad \Rightarrow \quad \text{C} - \text{C} = \text{C} = \text{N}
\end{align*}
\]

This accounts for the depression of the normal additive reactivity of the olefinic bonds towards electrophilic reagents since the provision of unshared electrons is made more difficult. At the same time, a point of attack is provided for a nucleophilic reagent at the carbon atom situated in the \(\beta\)-position with respect to the carbonyl or nitrile group.

By analogy, we should expect a similar electron shift away from the double bond to occur in the molecule of tetrafluoroethylene. The following discussion shows that this electron shift is also to be expected on theoretical grounds.

Consider first a monohalo-olefine, \(\text{CH}_2\text{CHX}\). The \(\text{C}-\text{X}\) bond in such a molecule will be formed by combination of a \(p\) atomic orbital of the \(\text{X}\) atom and a \(sp^2\) hybrid orbital of the carbon atom as shown in Figure 2. Owing to the greater electronegative character of the halogen atom than the carbon
FIGURE 7

ATOMIC ORBITALS IN A MONO-HALO OLEFINE
atom, the electrons forming the bond will be attracted towards the halogen. This effect, which is shown by the straight arrow (\rightarrow) in Figure 7, is equivalent to the Inductive Effect of the electronic theory, and will give rise to a dipole moment in the molecule. In methyl fluoride a similar effect will occur, and the dipole moment of 1.81 for methyl fluoride is a measure of the magnitude of this effect. This shift of electrons away from the carbon atom \( C_1 \) will result in a stronger attraction of this atom on the electrons forming the \( C=O \) bond. This secondary effect, which is represented by (\rightarrow) in the diagram, will lead to a deactivation of the double bond with respect to electrophilic reagents.

In addition to this shift of electrons away from the double bond, a second effect leading to a drift of electrons in the reverse direction will be expected to occur. This will arise from the sharing of the electrons in the \( p \) orbital of the \( X \) atom with the \( \pi \) orbital of the carbon atom \( C_1 \). This effect must also be relayed to the \( \pi \) orbital of the carbon atom \( C_2 \), and is represented by the curved arrows (\rightarrow) and (\rightarrow) in the diagram. The inductive effect of the \( X \) atom, which tends to increase the electron attracting power of the carbon atoms, would be expected to support this second effect, which is equivalent to the Mesomeric Effect of the electronic
As has already been stated, the inductive effect leads to deactivation of the double bond towards electrophilic reagents. The mesomeric effect, however, leads to an increase in the electron availability in the double bond, and hence an increase in reactivity towards electrophilic reagents would be expected.

The question now arises as to which of these two effects is the most important. In methyl fluoride, only the inductive effect will arise, since the carbon atom has the sp$_3$ hybrid form, and no π orbitals. This molecule has a dipole moment of 1.81. In fluorobenzene, however, circumstances are somewhat similar to those found in a monohalo-olefine, since in addition to the inductive effect of the fluorine atom, the mesomeric effect may also occur by drift of electrons from the p orbitals of the fluorine atom to the π orbitals of the benzene ring. This molecule has a dipole moment of 1.57, and hence it can be concluded that whilst the mesomeric effect reduces the dipole moment of fluorobenzene, it is not sufficient to cancel out completely the inductive effect. By analogy we may expect a similar state of affairs in the molecule CH$_2$;CHX, and the combined effects will be expected to lead to deactivation of the double bond.

In the presence of the electric field of a reagent
molecule, such as that surrounding a molecule of bromine, the drift of electrons from the p orbital of the X atom to the \( \pi \) orbitals of the carbon atoms may be enhanced. This is a polarizability effect which is equivalent to the Electromeric Effect of the electronic theory. The fact that bromine is less reactive towards vinyl bromide than ethylene (67) indicates that in the above reaction the inductive effect is greater than the combined mesomeric and electromeric effects.

In a symmetrically substituted dihalo-olefine, the inductive effects of the two halogen atoms will tend to deactivate the double bond with respect to electrophilic reagents, whereas the mesomeric effects will increase the electron availability in the double bond and hence will tend to increase its reactivity towards electrophilic reagents. Since, in the case of a monohalo-olefine, the combined effects appear to give rise to deactivation of the double bond towards electrophilic reagents, the presence of two symmetrically substituted halogens in an olefine should give rise to a greater deactivation with respect to such reagents.

From the work of Henne and Arnold (60) it appears that in a symmetrically substituted dihalo-olefine appreciable deactivation of the double bond with respect to an electrophilic reagent does, in fact, occur. Thus, whereas hydrogen
fluoride adds readily to ethylene under pressure, and a
certain amount of addition to monohalo-olefines also occurs
under similar conditions, it was found that no addition took
place when the compound CHCl=CHCl was heated with hydrogen
fluoride under pressure in the absence of a catalyst.

In the molecule of tetrafluoroethylene, therefore, the
combined inductive effects of the four fluorine atoms may
be expected to be much greater than the combined mesomeric
effects. Hence, tetrafluoroethylene may be expected to be
much less reactive towards electrophilic reagents than
ethylene. The withdrawal of electrons away from the double
bond may, at the same time, be expected to give rise to a
tendency for tetrafluoroethylene to react with nucleophilic
reagents. As has been shown above, experimental evidence
supports these expectations.

The polymerization of tetrafluoroethylene—Pure tetrafluoro-
ethylene is relatively stable, but in the presence of traces
of oxygen, peroxides (68), and Friedel-Crafts type catalysts
such as boron trifluoride and zinc chloride (69)(70), the
gas polymerizes readily under pressure to give the high
molecular weight solid polymer known commercially as 'P.T.F.E.'
and 'Teflon'.

Haszeldine (55) found that the polymerization of
tetrafluoroethylene and also of ethylene could be brought
about by trifluoromethyl radicals produced photochemically or thermally from iodotrifluoromethane. The principal products formed on heating, or irradiating tetrafluoroethylene in the presence of iodotrifluoromethane are long chain polymers. Under similar conditions ethylene reacts less readily to give mainly short chain polymers.

The work of Rael and Danby (71) shows that the rate of polymerization of tetrafluoroethylene induced by acetaldehyde photolysis is much greater than that of ethylene under the same conditions. A polymer containing approximately 26 fluoroethylene units is obtained, whereas with ethylene, the maximum degree of polymerization observed corresponds to approximately 3 ethylene units per molecule.

Rael and Danby pointed out that at the temperature (approximately 300°C.) at which the experiments were carried out, the formation of high polymers from ethylene was not to be expected, since at these temperatures polyethylene decomposes readily, whereas polytetrafluoroethylene is quite stable.

They suggested that the observed acceleration of the rate of aldehyde photolysis in the presence of tetrafluoroethylene as compared with ethylene, was due to the greater reactivity of the trifluoromethyl radicals as
compared with methyl radicals. It was concluded that a trifluoromethyl radical could be produced by a chain transfer reaction and that this radical subsequently induced the decomposition of a molecule of acetaldehyde into carbon monoxide and methane without itself suffering any change, i.e.

\[ \text{CH}_3 + (\text{C}_2\text{F}_4)_n = R \]

\[ R = \text{Product} + \text{CF}_3 \]

\[ \text{CF}_3 + \text{CH}_3\text{CHO} = \text{CF}_3 + \text{CH}_4 + \text{CO} \]

**Tetrafluoroethylene polymer:** The polymer 'Teflon' is a white solid with a high softening point, and a high resistance to chemical attack (72). No solvent for it has been reported. Although the polymer is quite stable at the normal fabrication temperatures of 330° to 360°C., it undergoes degradation to low molecular weight fluorocarbons if it is maintained at temperatures above 360°C. (73). The extent and rate of this degradation increases with temperature.

Lewis and Naylor (74) found that the products of pyrolysis of 'Teflon' at temperatures between 600° and 700°C, and at pressures from 5 to 760mm. were tetrafluoroethylene, hexafluoropropene (incorrectly assumed to be hexafluorocyclopropane), and octafluorocyclobutane, in varying amounts, depending on the experimental conditions.

It was concluded that the polymer decomposes by
splitting off units of the original monomer from a degrading fragment, and that these monomer units subsequently undergo secondary reactions to form higher molecular weight compounds.

In contrast to the high thermal stability of poly-tetrafluoroethylene, polyethylene decomposes at temperatures above 290°C. (75). The products of mild degradation are plastics similar to the original polyethylene, more extensive degradation yields semi-solid pastes or liquids. Gaseous products are only formed in appreciable quantities at temperatures above 370°C., and even at these temperatures ethylene is only a minor constituent of the volatile products. In runs carried out at 315° and 360°C., a decrease in reaction rate was observed as the amount of degradation increased. To explain these observations it was suggested that pyrolysis proceeded by a chain reaction started at a peroxide or other weak link present in very low concentration in the polymer molecule, and is propagated mainly through the points of branching in the polymer chain.

The greater stability of 'Teflon' as compared with polyethylene, and the difference in the nature of the degradation products of the two polymers, suggests that there are no weak links present in a molecule of 'Teflon' at which chain reactions may be initiated.
(v) Hexafluoropropene.

The compound was prepared by Henne and Waalkes (76) using the general method of reduction of 1:2-dichloro-hexafluoropropene with zinc in alcohol. Brice, Pearson, and Simons (77) obtained the same product by reduction of the dibromo- derivative with zinc in acetic acid.

The compounds prepared by the pyrolysis of mono-chlorodifluoromethane (48) and of tetrafluoroethylene (54) and by the thermal decomposition of tetrafluoroethylene polymer (73)-(74) were originally reported as hexafluorocyclopropane. Young and Murray (78) compared the properties of a sample of C₃F₆ obtained by the pyrolysis of tetrafluoroethylene polymer with those of a sample of hexafluoropropene obtained by dechlorination of 1:2: dichlorohexafluoropropene with zinc in alcohol. The boiling points and freezing points of these two compounds agreed within the limits of experimental error. Infra-red absorption curves of the two samples were found to be identical, and chlorination of the two products gave identical dichlorides which were different from the dichloride obtained by chlorination of the compound \( \text{H(CF}_2\text{)}_3\text{Cl} \). On this evidence Young and Murray concluded that the product of pyrolysis of tetrafluoroethylene polymer was hexafluoropropene and not hexafluorocyclopropane.
The physical and chemical properties of the samples of $\text{C}_3\text{F}_6$ prepared by the methods mentioned above are all identical with those of hexafluoropropene, and hence it may definitely be concluded that these samples are also of hexafluoropropene and not of hexafluorocyclopropene. This conclusion is supported by measurements of Raman and infrared spectra carried out by Edgell (79) and by electron diffraction data obtained by Buck and Livingston (80).

Further support for this conclusion is obtained from the work of Atkinson (1). He found that hexafluorocyclopropane prepared by the mercury photosensitized reaction of tetrafluoroethylene had different properties from those of hexafluoropropene, in particular, the cyclic fluorocarbon did not react with bromine. All the samples of $\text{C}_3\text{F}_6$ referred to above react readily with bromine, and can therefore be concluded to consist principally of hexafluoropropene.

Henne and Waalkes (76) reported the following physical properties for hexafluoropropene,

- freezing point, $-156.2^\circ\text{C}$.
- boiling point, $-29.4^\circ\text{C}$.

More recently the following values have been obtained, (5)

- freezing point, $-158.1^\circ\text{C}$.
- boiling point, $-28.2^\circ\text{C}$ (at 744.3 mm. pressure)
Buck and Livingston (80) found that the electron diffraction data for hexafluoropropene could best be interpreted by means of a 'strained' model in which none of the fluorine atoms was in the plane determined by the three carbon atoms. Such a molecule would be expected to have a different reactivity to that of propene which has all the atoms in one plane except the hydrogen atoms in the CH₃ group.

Although the evidence available is not sufficient to make a close comparison between the reactivities of propene and hexafluoropropene, it appears that both compounds react similarly with the halides, but that hexafluoropropene is much less reactive towards the hydrogen halides than propene. Thus hexafluoropropene reacts readily with chlorine and bromine to form the corresponding dihalides (5). When a mixture of hexafluoropropene and aqueous hydrogen fluoride are heated to 200°C. under pressure, addition takes place to give heptafluoropropane (81). At 90°C. in the presence of a carbon-calcium sulphate catalyst, hexafluoropropene reacts with hydrogen bromide to give the compound $C_3F_6HBr$ (62). Hexafluoropropene is readily oxidised by a solution of potassium permanganate in acetone (5).

Owing to the strong electron attracting property of the fluorine atom, we should expect that a CF₃ group attached to a carbon atom adjacent to a double bond would tend to
deactivate the double bond in a similar manner to a fluorine atom. The lack of reactivity of hexafluoropropene towards electrophilic reagents such as the hydrogen halides shows that a deactivation of the double bond similar to that observed in tetrafluoroethylene, does in fact occur.

(vi) The octafluorobutenes.

Octafluorobutene-1, b.pt. 4.8°C., is reported to be the principal product of pyrolysis of tetrafluoroethylene at 750°C. (5). It is also obtained in good yield from the pyrolysis of octafluorocyclobutane at 700°C. (5). The structure of the compound obtained by the above methods was deduced from the melting point of the dichloride, and the boiling point of the fluorine addition compound, together with the fact that the gas reacts readily with a solution of potassium permanganate in acetone.

Henne and Newby (82) obtained octafluorobutene-2 in good yield by dechlorination of the compound CF₃-CFCl-CFCl-CF₃ using zinc and alcohol. Their attempts to prepare octafluorobutene-1 by a similar method were unsuccessful, as rearrangements always occurred in the chloro-fluoro-compounds formed in the intermediate stages. Henne and Newby reported that the product obtained by the method outlined above was a cis-trans mixture of octafluorobutene-2 boiling over the range 0.4° to
Octafluorobutene-1 and octafluorobutene-2 have been reported to react with chlorine to give the corresponding dichlorides when refluxed with the halogen with strong irradiation. Octafluorobutene-2 also reacts with bromine under similar conditions to give the dibromide. Both compounds are readily oxidized by a solution of potassium permanganate in acetone (5).

(c) The perfluorocycloalkanes.

(i) Hexafluorocyclopropane.

As mentioned earlier, hexafluoropropene has been wrongly reported as hexafluorocyclopropane by a number of authors. The cyclic compound was obtained by Atkinson (1) as one of the products of the mercury photosensitized decomposition of tetrafluoroethylene.

The following physical properties were reported (1),

melting point, \(-80^o \pm 1^o C\).

boiling point, \(-33^o \pm 1^o C\).

The vapour pressure of the liquid over the range \(-80^o\) to \(-35^o C\) is given by

\[
\log_{10} P_{\text{mm}} = 7.746 - 1168/T
\]

latent heat of vaporization \(5354\) cal. per mole

Trouton’s constant \(22.3\)
The gas was found to be completely unreactive towards bromine, in contrast to hexafluoropropene which reacts slowly to give the dibromo derivative.

Hexafluorocyclopropane is much more stable than the corresponding cyclic hydrocarbon. Thus, cyclopropane reacts with bromine, ring opening and addition occurring to give 1:3:6 dibromopropane(63).

The mercury photosensitized polymerization of cyclopropane has been studied by Cunning and Steacie (64), who found that a steady reaction occurred, the principal product of which was a liquid polymer with the formula \((C_3H_6)_n\). A mechanism was proposed for the polymerization involving the initial formation of an energy rich trimethylene biradical by the reaction

\[
C_r + Hg(3P) = R_1^* + Hg(S_0)
\]  

The activated radical can either reform cyclopropane upon collision, or form a higher biradical,

\[
R_1^* + C_r = 2C_r
\]

\[
R_1^* + C_r = R_2^* \text{ etc.}
\]

In the above equations \(R_1 = -(CH_2)_3-\) \(R_2 = -(CH_2)_6-\), and \(C_r\) = cyclopropane.

It was suggested that chain termination occurred when the polymer biradical could no longer furnish sufficient energy to break the C-C bond in cyclopropane. The radical
FIGURE 8.

ATOMIC ORBITALS IN HEXAFLUOROCYCLOPROPANE.
may then stabilize itself by a proton shift. Gunning and Steacie concluded that reaction (2) is at least 43 times faster that reaction (3).

In contrast to this ready polymerization of cyclopropane, it was found that with hexafluorocyclopropane, the rate of the mercury photosensitized polymerization was almost negligible (1).

The reason for the lack of reactivity of hexafluorocyclopropane becomes apparent when we examine the structure of the molecule. On the basis of the physical and chemical properties of cyclopropane it appears that the CH$_2$ groups in the molecule resemble the CH$_2$ groups of ethylene rather than those found in a paraffin chain. Walsh (95) concluded that the carbon atoms in cyclopropane are of the sp$^2$ hybrid type and that molecular orbitals are formed by overlap of these atomic orbitals, and also of the 2p atomic orbitals of the carbon atoms as shown in Figure 8. A, B, C, and D are CH$_2$ planes at 90$^\circ$ to the paper.

The C-C bonds in cyclopropane thus resemble the double bond in ethylene, and addition of electrophilic reagents such as bromine will take place in a manner similar to that occurring with an olefine, i.e., by attack of a bromine molecule on the weakly bound electrons in the molecular orbitals formed from the carbon 2p atomic orbitals.
It seems reasonable to assume that the molecular orbitals formed from the atomic orbitals of the three carbon atoms in hexafluorocyclopropane are similar to the corresponding orbitals in cyclopropane. On replacing the hydrogen atoms of cyclopropane by fluorine, two new effects will arise. Firstly, we should expect the inductive and mesomeric effects of the fluorine atoms to give rise to a decrease in reactivity of the molecule towards electrophilic reagents, as compared with cyclopropane, corresponding to the decrease in reactivity of tetrafluoroethylene as compared with ethylene. The fact that hexafluorocyclopropane is completely unreactive towards bromine supports this theory.

A second effect which will also tend to reduce the reactivity of hexafluorocyclopropane towards molecules such as bromine will arise from the steric hindrance caused by the fluorine atoms. This steric effect will tend to shield the weakly bound electrons of the carbon atoms from attacking molecules as shown in Figure 8, where the dotted lines represent atomic 2p orbitals of two of the fluorine atoms and the sp2 hybrid orbitals of two of the carbon atoms. These 'dotted' orbitals are not in the plans of the paper.

In the mercury photosensitized polymerization of cyclopropane, only approximately 2% of the collisions between
a trimethylene biradical and a cyclopropane molecule result in the formation of a higher biradical according to reaction (3). In these collisions the trimethylene biradicals must attack the weakly bound electrons in the C–C bonds. In the case of hexafluorocyclopropane, it will clearly be more difficult for a C\textsubscript{3}F\textsubscript{6} biradical to approach these electrons and hence we should expect that the percentage of collisions leading to reactions of type (3) would be negligible. Thus little, if any, polymerization should occur in the mercury photosensitized reactions of hexafluorocyclopropane. As has already been mentioned, the experimental results show that with hexafluorocyclopropane, the amount of the mercury photosensitized polymerization which occurs is, in fact, negligible.

(ii) Octafluorocyclobutane.

This compound is formed by the pyrolysis of tetrafluoroethylene (5)(54), monochlorodifluoromethane (48), and of tetrafluoroethylene polymer (73)(74).

Benning and Downing (86) reported the following physical properties,

freezing point, \(-40.7^\circ\text{C}\).
boiling point, \(-4.7^\circ\text{C}\).

They found that the gas decomposed appreciably at temperatures above \(200^\circ\text{C}\). in steel or bronze reaction vessels,
when it was heated under pressure. It was stable in a nickel vessel at temperatures below 400°C. At 700°C, octafluorocyclobutane has been found to decompose rapidly to give octafluorobutene-1 and hexafluoropropene together with small amounts of high molecular weight compounds (5). The gas does not react with bromine or chlorine, and does not decolourise a solution of potassium permanganate in acetone (5).

Lemaire and Livingston (57) giving preliminary results of an electron diffraction investigation conclude that the four membered carbon ring of octafluorocyclobutane is non-planar. In the case of cyclobutane, spectroscopic evidence favours a planar ring (66). It appears probable that the non-planar ring in octafluorocyclobutane may be attributed to repulsions between fluorine atoms attached to different carbon atoms. The distortions observed in the molecule of hexafluoropropene have been explained on the basis of similar repulsive forces between fluorine atoms (57). It is interesting to note that in both molecules the closest distance of approach of fluorine atoms attached to different carbon atoms is about 2.70 Å, which is twice the van der Waals radius of fluorine. The repulsive forces between fluorine atoms attached to different carbon atoms may also be responsible for the slightly higher value for the C-C distance found in octafluorocyclobutane as compared with the normal value found in most
Further support for the non-planar ring structure of octafluorocyclobutane is obtained from the work of Edgell and Weiblen (89) who found that the infra-red and Raman spectra are best explained on the basis of a non-planar ring. Claassen (90), however, has studied the vibration spectra of octafluorocyclobutane and assigned frequencies on the basis of a planar model.

As has already been mentioned, the properties of cyclopropane are best explained by assuming that the orbitals in the CCC ring are formed by overlap of the orbitals of three carbon atoms in the sp\textsubscript{2} hybrid state. From the little experimental evidence available it appears that in cyclobutane however, the carbon valencies towards hydrogen are nearer the sp\textsubscript{3} than the sp\textsubscript{2} hybrid type, and that the orbitals in the four membered ring contain no loosely bound \textit{H}-type electrons. Thus, whereas cyclopropane reacts with bromine to yield 1:3: dibromopropane, cyclobutane yields substitution products if any reaction occurs. Similarly, hydrogen bromide readily adds on to cyclopropane to give propyl bromide, but it does not attack cyclobutane. Further evidence in favour of the sp\textsubscript{3} type hybrid carbon orbitals in cyclobutane is obtained from the work of Wilson (88). He studied the infra-
Infrared and Raman spectra of cyclobutane and assigned frequencies, on the basis of a tetrahedral HCH angle.

In the case of octafluorocyclobutane, the lack of reactivity of the molecule towards reagents such as bromine does not indicate the absence of weakly bound π-type electrons, since it has been noted that in hexafluorocyclopropane the fluorine atoms tend to protect the weakly bound electrons in the 2p atomic orbitals, and also to deactivate the molecule towards electrophilic reagents. Similar effects would be expected to occur in the molecule of octafluorocyclobutane.

It has been found that the FCF angle in octafluorocyclobutane lies between 107° and 112° (87), and this suggests that in this molecule the carbon valencies towards fluorine are nearer to the sp3 than the sp2 hybrid type. This evidence is inconclusive, however, since in tetrafluoroethylene, where the carbon valencies towards fluorine are of the sp2 hybrid type, values of 110° and 114° have been reported for the FCF angles (91) and these figures are closer to the tetrahedral angle than the trigonal angle. Thus, although, by analogy with cyclobutane, the molecular orbitals in octafluorocyclobutane may be formed from carbon atomic orbitals which are nearer the sp3 than the sp2 hybrid type, the exact nature of the atomic orbitals is uncertain.
Several general methods have recently been developed for the preparation of the saturated fluorocarbons. These include the catalysed fluorination of carbon and of hydrocarbons. A number of physical properties of the lower members of this series have been reported. These compounds show a marked stability as compared with their hydrocarbon analogues. This stability is probably due to the high C-F bond strength as compared with that of the C-H bond.

Certain general methods of preparing the perfluoroolefines have been developed, but since these methods require starting materials which are themselves difficult to prepare, the perfluoro-olefines are usually prepared by special methods.

Of the perfluoro-olefines, only tetrafluoroethylene has been studied in any detail. A number of physical properties of this compound are reported, but very few physical data are available for the higher homologues.

Tetrafluoroethylene appears to polymerize much more readily than ethylene to give a high molecular weight polymer which is much more stable than polyethylene.

A number of addition reactions occur with the perfluoro-olefines which are characteristic of substances containing a double bond. In general, the addition reactions occur less
readily than the corresponding reactions with hydrocarbon olefines, however, and a number of addition reactions occur which have no parallel in the chemistry of the hydrocarbon olefines. The difference between the chemical behaviour of the perfluoro-olefines and the hydrocarbon olefines may be attributed to the strong electron-attracting properties of the fluorine atoms and the overlap of the fluorine and carbon orbitals, and also the repulsions between fluorine atoms attached to different carbon atoms.

The cyclic fluorocarbons appear to be much more stable than their hydrocarbon analogues. This difference in stability appears to be due to steric effects of the fluorine atoms and also to the effects mentioned above.

At the time of commencement of the work described in this thesis, no accurate kinetic data for the thermal reactions of the perfluoro-olefines were available, and apart from the details given by Harmon (54), no systematic investigation of the pyrolysis of tetrafluoroethylene had been published.

The work described in this thesis is an examination of the thermal reactions of tetrafluoroethylene. The kinetics of the reactions occurring at low temperatures have been studied in detail, and the heat data derived from this work have been used as a basis for a comparison between ethylene and tetrafluoroethylene.
2. EXPERIMENTAL.

(a) Outline of experimental procedure.

A small cylinder of tetrafluoroethylene was kindly supplied for the purpose of this research by I.C.I. (General Chemicals Division) Ltd. Portions of this gas were purified in a flow system, and the purified gas was passed through a reaction vessel heated in an electric furnace. The products of pyrolysis were collected in a series of traps, and were subsequently analysed by low temperature fractional distillation. The products were then separated into their individual components by further fractional distillation and these individual components were purified by fractionation between traps. Portions of the purified samples were used for the determination of physical and chemical properties.

(b) The flow apparatus for the thermal decomposition of tetrafluoroethylene.

(i) Apparatus.

The apparatus was similar to that used for the study of the thermal decomposition of ethylene (see page 19) except for the following minor alterations.

The wash-bottles A and B (Figure 1) were replaced by a single indicating wash-bottle containing water. The oxygen absorption vessel J was removed, and a small soda-glass trap was fixed between tap H and the calcium chloride
tube K. The phosphorus pentoxide tube L was omitted as it was found that tetrafluoroethylene reacts with phosphorus pentoxide, a colourless "gluey" mass being formed.

The silica reaction vessel used in the investigation of the thermal decomposition of ethylene was employed in the runs carried out below 600°C. Above 600°C, a steel tube 23 cm. in length and 3.4 cm. internal diameter was used. This tube was fitted with capillary inlet and outlet tubes 50 cm. in length. The ends of the capillary tubes were sealed into the glass tubing with picein. These picedined joints were kept cool by surrounding them with water jackets. The thermocouple was attached to the outside of the tube.

A small tube packed with glass wool was fixed between the reaction vessel and the collecting traps. This served to collect any polymer dust leaving the reaction vessel, and thereby prevented the contamination of the remainder of the apparatus.

(ii) Preparation of the apparatus.

The method of preparation of the apparatus was similar to that described on page 23. The trap between tap H and the calcium chloride tube was cooled to approximately -12°C in a bath of ice and freezing salt. This trap served to remove the stabilizer from the cylinder gas. The stabilizer
is added to the gas in the cylinder to remove traces of oxygen which catalyse the polymerization of tetrafluoroethylene at the high pressures existing inside the cylinder. It was therefore unnecessary to include the tube of activated copper in the purification train as the cylinder gas was free from oxygen.

(iii) **Procedure for operation of the flow apparatus.**

The procedure adopted for passing the gas through the flow apparatus and collecting the products was the same as that described on page 24. The condensable products of pyrolysis were analysed by fractional distillation in the low temperature distillation column. The non-condensible gas collected in the charcoal trap was transferred to a measuring burette by means of a Toepler pump, and its volume determined.

(c) **The electric furnace.**

(i) **Furnace construction and operation.**

In the investigation of the thermal decomposition of ethylene and of tetrafluoroethylene, the furnace used to heat the reaction vessels was of the wire-wound, horizontal, tubular type. A coil of nichrome wire was wound onto 17 inches of the length of a Mullite tube 2 feet in length and 1 inch internal diameter and $\frac{1}{8}$ inch thickness. Details of the method of winding are given below. The tube was packed into a Syndanyo box 18 inches in length, 8 inches wide, and 8 inches
deep, using crystalline alumina as the packing material. The two ends of the Mullite tube projected through holes cut in the centre of each end of the box. The heating coil was connected to the 230 volt a.c. mains through a Sunvic Energy Regulator.

The coil of nichrome wire was wound onto the Mullite tube in the following manner. Three layers of wet asbestos paper were first wrapped around the Mullite tube. The nichrome wire of 22 S.W. gauge (2.54 ohms per yard) was secured to the asbestos covered tube at a point 3½ inches from the end of the tube by means of a short length of nichrome wire wound tightly around tube and wire two or three times. The wire was fixed to the tube so as to leave a free end of wire approximately 2 feet in length. It was then wound evenly over the asbestos paper, care being taken to make the spacings between the individual coils as nearly equal as possible. The winding was continued until a coil of approximately 240 turns and 70 ohms resistance had been wound, covering 17 inches of the length of the Mullite tube. The wire was then secured to the tube as before, and was cut so as to leave a free end approximately 2 feet in length. A layer of asbestos string was wound tightly over the coil, leaving a 3½ inch length of the tube uncovered at each end. The two free ends of nichrome wire were doubled back, and each pair of strands was twisted together to give two double one foot lengths of wire. The ends of these double
lengths were connected to two terminals fixed in the side of the Syndanyo box. The terminals were connected through the Sunvic Energy Regulator to the a.c. mains.

The furnace required 5 to 6 hours to heat to the temperatures within the experimental range. The temperature at the centre of the reaction vessel could then be kept constant to ± 1°C. by occasional adjustment of the Sunvic Energy Regulator. After about 12 hours heating time, the temperature in the reaction vessel tended to settle to a steady value, and it could then be kept constant to ± 1°C. with very little adjustment of the Regulator.

The uniformity of the temperature inside the silica reaction vessel was checked with the furnace at a steady temperature within the experimental range. The temperature was found to be uniform along the middle 18cm. of the vessel, but a drop of 1½°C. occurred towards both ends of the vessel. This temperature drop was considered too small to warrant any further lagging of the furnace tube, in the flow experiments.

(ii) Temperature measurement.

The furnace temperature was measured using a chromel-alumel thermocouple in conjunction with a Dornan potentiometer. The thermocouple was constructed in the following manner. One end of a 3 foot length of chromel wire was joined to the end of a similar length of alumel wire by twisting the
ends together to give a double strand about \( \frac{1}{4} \) inch long. This joint was hammered gently to ensure a good contact between the wires. A sufficient number of porcelain insulators were slid over the wires to cover two thirds of the length of each wire.

The end of a 3 foot length of cotton covered copper wire was twisted around the end of the chromel wire, and a similar length of copper wire was joined to the free end of the alunel wire. Both of these joints were pushed into thin walled glass tubes 20cm. in length and 7mm. in diameter, the bottoms of which were sealed and drawn out to give very thin walled ends. The wires were sealed into the tops of the tubes with picein.

The two free ends of the lengths of copper wire were connected to the potentiometer, and the tubes containing the chromel-copper and alunel-copper junctions were placed in a beaker of ice. The chromel-alunel junction, forming the "hot" junction of the thermocouple, was placed inside the thermocouple well of the silica vessel. In the case of the metal vessel, the thermocouple was attached to the outside of the tube by means of asbestos string so that the end of the thermocouple was in the middle of the length of the tube.

The thermocouple was standardized against an accurate platinum-platinum/rhodium thermocouple over the
Plate 1. The distillation apparatus.
FIGURE 9.
DISTILLATION APPARATUS

Figure 1
To Tip Y
temperature range 300° to 800° C., the "hot" junctions of both thermocouples being placed side by side in the furnace tube. It was found that the temperature values given by the chromel-alumel thermocouple agreed with those given by the platinum-platinum/rhodium couple to within ± 0.5° C. The chromel-alumel thermocouple was therefore assumed to be accurate to within these limits over the temperature range 300° to 800° C.

(d) The distillation apparatus.

The condensable products of pyrolysis of ethylene and tetrafluoroethylene were analysed by fractionation in low temperature distillation columns of the Podbielniak type (92). The apparatus used is shown in Figure 9, and in Plate 1. The large column was designed for the fractionation of quantities of liquid up to 25ml. This column was used for the distillation of the products of pyrolysis of ethylene, and the purification of samples of tetrafluoroethylene. Liquid samples up to 5ml. in volume could be handled in the smaller column, which was used for the distillation of the products of pyrolysis of tetrafluoroethylene.

(i) The fractionating columns.

1. The large column.

The details of the construction of the large column are shown in Figure 10. The column was constructed
entirely of Pyrex glass, and was joined to the soda-glass inlet and take-off tubes by standard tapered joints sealed with pinein. The column tube was packed with a single coil of copper wire, and was surrounded by a silvered vacuum jacket. Two narrow unsilvered strips were left along the length of the jacket for observation purposes. The distilling bulb and precooiling tube were surrounded by a glass thimble, which was packed in glass wool in a wide Dewar vessel. This vessel also had two narrow unsilvered observation strips along its length, the glass wool packing being in two segments to allow a clear view of the distilling bulb.

Heat was supplied to the distilling bulb by means of a coil of 34 S.W.G. nichrome wire of 26 ohms resistance, wound around the bottom of the bulb as shown. The coil was connected in series with a variable rheostat and the 11 volt tappings of the secondary winding of a step-down transformer, the primary windings being connected to the 230 volt a.c. mains. A smaller coil of 34 S.W.G. nichrome wire, of 10 ohms resistance, was wound around the bottom of the pre-cooling tube as shown (Figure 10). This coil was connected in series with a switch, a variable rheostat, and the 4 volt tappings of the secondary winding of the step-down transformer. This coil was used to liquify any solid material in the pre-cooling tube at the commencement of the distillation, and prevented
any build up in pressure occuring in the pre-cooling tube. The small heating coil was also found to assist in the mixing and steady ebullition of the liquid in the distilling bulb.

The Pyrex glass cooling vessel was packed into the top of the vacuum jacket with asbestos wool and asbestos string. The space between the inner wall of this vessel and the column tube was filled with fine copper powder to ensure an efficient heat transfer.

The temperature of the vapour at the top of the column tube was measured by means of a copper-constantan thermocouple in conjunction with a Doran potentiometer. The thermocouple leads were sealed into the piccinied joint at the top of the column tube. The "cold" junction was fixed in a tube at room temperature.

2. The small column.

The details of the construction of the small column are given in Figure 11. The design of the distilling bulb was altered slightly from that in the large column, as it was found unnecessary to employ a pre-cooling tube when entering such small volumes of gas into the distilling bulb. The distilling bulb heater consisted of a coil of 34 S.W.G. nichrome wire of 14 ohms resistance. This was connected in series with a variable rheostat, and the 8 volt tappings of the secondary winding of the step-down transformer.
(ii) The collecting and measuring apparatus.

In order to reduce to a minimum the dead space from the thermocouple junction to tap D (Figure 9), this section of the apparatus was constructed of $\frac{1}{4}$ mm. bore capillary tubing. This reduced as much as possible the time lag between the measurement of the temperature of the vapour at the top of the column, and the passage of the vapour into the collecting vessels.

Either the small or the large column could be connected to the collecting apparatus by turning the capillary threeway vacuum tap C. The distillate could be collected in one of the $\frac{3}{4}$ litre bulbs A and B, or in the 750 ml. bulb C. The two large bulbs were used for all general purposes, the small bulb being employed when measurements of small volumes of distillate were required. No special precautions were taken to keep the receiving bulbs at a constant temperature, as sufficient accuracy was achieved without thermostating. A bulbed manometric manometer was used to measure the pressure of the distillate. This type of manometer restricted practically all the movement of mercury to the closed arm, thus facilitating the taking of pressure readings.

The apparatus was connected to a series of storage bulbs and the vacuum pump through tap G. The inlet tubes to the distilling bulbs were also connected to the vacuum pump.
(iii) Mode of operation of the large column.

The whole apparatus was evacuated by pumping, and tap C was turned so that the large column was connected to the collecting apparatus. The distilling bulb and pre-cooling tube were cooled by saturating the glass wool in the large Dewar vessel with liquid nitrogen. Tap A was then slowly opened to admit the products of pyrolysis to the distilling bulb, and was adjusted so that the pressure in the distilling column was always well below that beyond tap A.

The gases were cooled as they passed down the pre-cooling tube, and were condensed in the distilling bulb. Towards the end of the filling operation, the rate at which the gases passed into the distilling bulb slowly decreased, and the gases tended to solidify in the distilling bulb and pre-cooling tube. This reduced still further the rate of filling, and it was sometimes impossible to transfer the last traces of pyrolysis products to the distilling bulb.

On completion of the filling operation, tap A was closed, and the two heating coils were switched on. As the contents of the distilling bulb warmed up, the pressure in the column slowly rose until the column manometer indicated that a pressure of one atmosphere had been reached in the column. Further rise in pressure was prevented by blowing
liquid nitrogen from a Dewar flask into the cooling vessel at the top of the column. The vapours from the sample in the distilling bulb were condensed at the top of the column, and the liquid flowed down the column tube over the packing. The supply of current to the main distilling bulb heater was controlled so that the pressure in the column was maintained at one atmosphere without the addition of an excessive amount of liquid nitrogen to the cooling vessel.

The heating of the contents of the distilling bulb and the cooling of the top of the column was continued until the whole of the column tube packing was wet, and a steady reflux was taking place. The temperature at the top of the column was noted and distillation was commenced by slowly opening tap D to allow the fractionated vapour at the top of the column tube to pass into one of the receiving bulbs. The receiving bulb manometer indicated the pressure in this bulb. The temperature of the vapour at the top of the column was noted at frequent intervals, and the rate at which the vapours were collected in the receiving bulb was adjusted by varying the setting of tap D to give the best possible fractionation. The distillation rate was reduced to a minimum whenever the vapour temperature started to rise, and increased again when the temperature became steady.

Throughout the distillation, the pressure in the
column was maintained as near as possible to one atmosphere, and steady refluxing of the sample was continued by adjusting the heat input to the distilling bulb heater, and by cooling the top of the column. In this manner one component after another was distilled with sharp temperature rises between each fraction, until the complete sample was distilled or until an undistillable residue remained in the distilling bulb.

Frequent simultaneous readings of the temperature at the top of the column and the pressure in the receiving bulb were taken, and a graph of vapour temperature against pressure of the receiving bulb was plotted from the results obtained. The percentage composition of the products of pyrolysis was calculated using this graph.

(iv) The mode of operation of the small column.

The procedure adopted for the fractionation of the products of pyrolysis of tetrafluoroethylene in the small column was similar to that used when distilling the products of pyrolysis of ethylene in the large column. By omission of the pre-cooling tube, the complete sample could be condensed into the distilling bulb by saturating the glass wool packing in the Dewar vessel surrounding the distilling bulb, with liquid nitrogen. On completion of the filling operation, tap B (Figure 9) was closed, and the distilling bulb heater was switched on, tap C being turned to connect the small column
FIGURE 12

AUTOMATIC DEVICE FOR COOLING COLUMN HEAD.
with the collecting apparatus. The subsequent procedure was as described above.

(7) The semi-automatic device.

When large samples of gas were being purified by distillation, it was found convenient to make the large column semi-automatic by employing the device shown in Figure 12.

A piece of platinum wire was sealed into the open arm of the distilling column manometer at a point well below the atmospheric pressure level, and a length of copper wire was joined to the end of the platinum wire. A second length of copper wire was pushed down into the open arm of the manometer until its end was at a point approximately 1 cm. above the atmospheric pressure level. The two lengths of copper wire were then connected in series with a resistance, a relay switch, and the 110 volt a.c. mains, to form circuit B (Figure 12). The other side of the relay switch was connected in series with the 250 volt a.c. mains and the coil of a Heju gas regulator, to form circuit A. The tube at the top of the gas regulator was connected to an air supply, through a pressure control valve. The air passed out of the regulator either through tube A or tube B, depending on whether circuit A was closed or open. Tube B was connected to a Dewar vessel containing liquid nitrogen, and a tube extending to the bottom of this vessel was connected to the cooling vessel at the top
of the distilling column.

When the distilling column was at, or below atmospheric pressure, circuit B was open and circuit A was closed. The compressed air then left the gas regulator through the by-pass tube A. When the mercury in the open arm of the distilling column manometer contacted the copper wire, circuit B was closed, and the relay switch opened circuit A. With circuit A open, the compressed air passed out of the gas regulator through tube B, and liquid nitrogen was blown into the cooling vessel. The top of the distilling column was thereby cooled, and the pressure inside the column decreased. The mercury level in the open arm of the distilling column manometer dropped, and circuit B was thereby opened. This closed circuit A. The compressed air then passed out through the by-pass tube A, and the supply of liquid nitrogen to the cooling vessel was cut off.

The distilling column could be run automatically by means of this device, for an appreciable time. This was very convenient when large samples of gas were being purified by distillation. It was, however, necessary to adjust the pressure control valve from time to time, to ensure that sufficient liquid nitrogen was blown over into the cooling vessel to reduce the pressure in the distilling column to just below one atmosphere when required.
FIGURE 13
VAPOUR PRESSURE APPARATUS.

FIGURE 14.
DETAILS OF COOLING VESSEL AND THERMOCOUPL.
(c) The measurement of vapour pressure.

(i) The apparatus and mode of operation.

The apparatus used for the measurement of vapour pressures is shown in Figure 13. It was constructed entirely of soda-glass. The liquid whose vapour pressure was to be measured was contained in a small bulb of 1.4cm. diameter, which was connected to the manometer B of internal diameter 0.3cm. This manometer stood beside and in the same trough as a similar manometer A, which was permanently under high vacuum. The mercury levels were read to ± 0.025cm. by means of a glass scale placed behind the manometers.

A suitable quantity of gas was condensed into the small bulb, and the bulb was surrounded by a cooling bath as shown in Figure 14. The Pyrex Dewar vessel which contained the cooling liquid had two narrow unsilvered observation strips along its length. The cooling bath was stirred mechanically by means of a small wooden stirrer connected to a motor. The temperature of the bath was measured using a copper-constantan thermocouple in conjunction with a Doran potentiometer. The thermocouple was fixed in the bath so that its end was as near as possible to, but not in contact with the small bulb. The "cold" junction of the thermocouple was placed in a beaker filled with ice. A full description of the thermocouple is given below.
Plate 2. The Vapour Pressure Apparatus.
Figure 15
The Isoteniscope

Figure 15B
Internal Thermocouple
The rate of rise in temperature of the cooling bath was made as slow as possible by using a large volume of cooling liquid, and by covering the top of the Dewar vessel with a piece of asbestos board. Frequent simultaneous readings of bath temperature and vapour pressure were taken as the temperature of the cooling bath rose. A liquid pentane bath was used over the temperature range $-135^\circ$ to $-100^\circ$C., and a bath of acetone plus ether was employed at temperatures above $-110^\circ$C.

In the apparatus used initially, one junction of a copper-constantan thermocouple was placed inside the small bulb as shown in Figure 15a. The copper and constantan wires were sealed into the side arms with pinein. This "internal" thermocouple was found to give accurate temperature readings when the small bulb was half filled with the liquid under examination. With solids or small volumes of liquids, however, erroneous temperature readings were obtained. This was probably due to poor contact between the material and the thermocouple junction. After a number of trial runs, this design was rejected in favour of that shown in Figure 14.

The isoteniscope shown in Figure 15 and in Plate 2, was used to measure the vapour pressure of very small samples of material. The sample of gas to be examined was condensed into the small bulb, and mercury was introduced into the
U-shaped manometer by rotating the small bulb containing mercury about the B10 joint. The mercury levels in each arm of the manometer were read by means of a scale placed behind the manometer. The bulb was surrounded by a cooling bath as shown in Figure 14, and simultaneous readings of bath temperature and vapour pressure were taken over a range of temperature.

When the vapour pressure measurements had been completed, the mercury in the manometer was returned to the small bulb by slowly rotating the apparatus in a clockwise direction about the B14 joint.

(ii) The Copper-Constantan Thermocouple.

A length of thin cotton-covered copper wire was welded to each end of a length of thin constantan wire. One junction was pushed into the thin walled glass tube A (Figure 14) which was drawn out at the bottom to give a very thin walled end. The wires were sealed into the top of the tube with picein. The other junction was pushed through the tube B, until it protruded about 0.5 cm. beyond the end of the tube. The wires were sealed into the bottom of the tube B using a cement composed of magnesium oxide, magnesium chloride, and silica, and into the top of the tube with picein. The two free ends of the copper wire were connected to the potentiometer.
(iii) Calibration of the thermocouple.

The procedure adopted was similar to that recommended by Farkas and Melville (93). A graph of voltage against temperature was plotted using the values given by Buffington (94) for the E.M.F. of a copper-constantan thermocouple with one junction at 0°C. The voltage of the thermocouple at several standard temperatures was obtained, and each figure was subtracted from the value given for the same temperature on the standard graph. The differences were plotted against the actual voltage of the thermocouple, and the points obtained gave a good straight line. In use, a correction figure was obtained from this graph and was applied to the measured voltage. The corrected voltage figure was used to find the temperature on the standard graph.

The standard temperatures were obtained in the following manner. A sample of pure ethylene was transferred to the small bulb of the vapour pressure apparatus, and the bulb was surrounded by a bath of melting pentane. Simultaneous readings of vapour pressure and thermocouple voltage were taken at a number of points between approximately -135°C and -115°C. The temperature of the bath was obtained from the vapour pressure figures by reference to the values quoted by Farkas and Melville.

A further fixed point was obtained by surrounding the
Figure 16

THE STANDARD VOLUME VESSEL.

Figure 17

APPARATUS FOR GAS VOLUME MEASUREMENT.
thermocouple with a Dewar vessel filled with finely powdered solid carbon dioxide. The method recommended by Scott (95) was used to ensure that the solid carbon dioxide was at its equilibrium sublimation temperature of -78.5°C.

A heating coil of 100 ohms resistance connected in series with a switch and a 25 volt supply, was placed in the bottom of the Dewar vessel. This coil was switched on for a few minutes before taking the temperature reading. A steady stream of carbon dioxide vapour was thereby evolved, and air was excluded from the Dewar vessel, giving the required conditions for the equilibrium sublimation temperature.

A final fixed point was obtained by placing the thermocouple in a water bath at approximately 20°C. The thermocouple voltage was noted, and the temperature of the bath was measured with an accurate mercury thermometer.

(f) Volume measurements and the determination of molecular weights.  

(i) The standard volume vessel.

A tube H (Figure 16) 15cm. in length, and 1.8cm. internal diameter, and a 2mm. bore vacuum tap J, were joined to the 750ml. bulb G. A short length of 1mm. bore capillary tubing was joined to the arm of the vacuum tap J as shown. The end of this capillary tube was sealed with a little picein. The bulb and its attachments were weighed on a large balance to ± 50 mg. and the whole was then filled with water up to
not including the barrel of the vacuum tap. The vessel was placed inside the balance case and left for one hour to allow the water to come to the temperature in the balance case. Any water which had expanded into the barrel of the tap was removed by inserting a strip of filter paper into the arm of the tap. The temperature inside the balance case was noted, and the vessel was then reweighed full of water. The weight of the water at a known temperature was evaluated, and the volume of the vessel at 20°C was calculated from this figure, using the calibration table for volumetric apparatus given by Kolthoff and Sandell (96).

The vessel was dried, and the picein seal at the end of tube K was removed. The vessel was then joined to the vacuum system at Y (Figure 17). A manometer A of 6mm internal diameter was joined to the capillary tube K at X with a length of 1mm bore capillary tubing. The volume of the bore of the capillary tubing between X and A was determined from its length and internal diameter, and this volume was added to the volume of the vessel as obtained above. The manometer A stood beside and in the same trough as a similar manometer B, which was permanently under high vacuum.

(ii) The measurement of gas volumes.

The volumes of samples of gas were measured to an accuracy of ±0.1 ml. in the following manner. A sample
of gas was condensed into the tube H, tap J was closed, and
the tube and its contents were allowed to warm to room temperature.
The heights of the mercury in A and B were then read to ± 0.01cm.
by means of a cathetometer. The room temperature was noted,
and the volume of the space between the end of the capillary
connecting tubing and the surface of the mercury in A was
determined from the length of this portion of the manometer
and the known diameter of the manometer tubing. This volume
was added to the known volume of the vessel plus capillary
connecting tubing. The volume of the sample of gas at N.T.P.
was calculated from the results obtained.

(iii) The determination of molecular weights of condensible
gases.

The molecular weights of the condensible products
of pyrolysis of tetrafluoroethylene were obtained from
vapour density figures, which were determined in the following
manner.

A gas density bulb F (Figure 17) of 120ml. capacity
was fitted with a 1mm. bore vacuum tap E and a B14 standard
joint L as shown. The bulb was attached to the vacuum system
at D, and evacuated by pumping. The bulb was detached from
the vacuum system, the grease on the joint L was removed,
and the tube was wiped with a soft cloth. The tube was then
weighed to ± 0.1mg; a counterpoise of approximately the same
size as the bulb F was placed on the opposite balance pan.

The gas density bulb was reattached to the apparatus, and a portion of the gas (not more than 125 ml.) whose vapour density was to be determined was condensed into the bulb. Taps E and C were closed, and the bulb and its contents were allowed to warm to room temperature. The bulb was then wiped and reweighed. The known weight of gas in the bulb was transferred to the standard volume vessel, and its volume was determined as described above. The volume of the sample at N.T.P. was calculated, and from the known weight of the gas, the vapour density and hence the molecular weight of the compound were calculated.

(iv) The determination of the molecular weights of the non-condensable gases.

The molecular weights of the non-condensable gases were also obtained from vapour density figures, determined in the following manner.

A small amount of charcoal was introduced into the bulb F, and was activated by heating under vacuum at 300°C, for approximately 24 hours. The vapour density bulb and activated charcoal were weighed as described above, and a sample of the non-condensable gas to be examined was absorbed in the activated charcoal cooled in liquid nitrogen. The bulb was allowed to warm to room temperature, and it was
Plate 3. The Gas Analysis Apparatus.
FIGURE 18
GAS ANALYSIS APPARATUS

FIGURE 19
SHEPHERD BUBBLING TYPE ABSORPTION VESSEL
then reweighed. The increase in weight was equal to the weight of non-condensible gas absorbed by the charcoal.

On warming the charcoal in F, the gas was evolved, and its volume was measured by transferring it in portions to the burette of the gas analysis apparatus. From the volume and weight of the sample, the vapour density and hence the molecular weight of the non-condensible gas were calculated.

(g) The gas analysis apparatus for the examination of the products of pyrolysis of tetrafluoroethylene.

In the study of the thermal decomposition of tetrafluoroethylene, the gas analysis apparatus was used for two purposes;-

(1) To confirm the presence of carbon monoxide in the non-condensible products, by absorption in acid cuprous chloride solution, and

(2) to test the various fluorocarbons formed for unsaturation.

(i) Apparatus.

The gas analysis apparatus is illustrated in Figure 18 and in Plate 3. It was constructed entirely of soda-glass except for the Pyrex absorption vessel G. The apparatus up to tap 5 was the same as that described on page 27, and the absorption vessels E and F were similar to the vessel J in Figure 3. E and F were joined to the 1mm. T-bore taps
5 and 6 by means of tapered joints.

One limb of the Shepherd bubbling type absorption vessel was connected to tap 7, the other limb being open. The volume of each limb was approximately 100ml. The vessel is shown in greater detail in Figure 19. The specially designed capillary tap 7 had a double bore solid key. The single arm on one side of the tap was joined to the apparatus by means of a short length of rubber pressure tubing, which was secured at each end by copper wire. One of the two arms on the other side of the tap was joined to the top of the closed limb. The other arm was sealed into the vessel, and extended nearly to the bottom of the closed limb. A 20mm. diameter, porosity 2, sintered disc was sealed into the end of this arm as shown.

(ii) Reagents.

Bromine solution (for unsaturation tests). 30g. of potassium bromide were dissolved in 100ml. of distilled water and 14ml. (44g.) of bromine were added to the solution. The mixture was shaken in a closed bottle until the bromine had dissolved.

Acid cuprous chloride solution (for carbon monoxide absorption). 1 litre of acid cuprous chloride solution was prepared by dissolving 135g. of cuprous chloride in 450ml. of distilled water, and then slowly adding, with constant stirring, 500ml. of concentrated hydrochloric acid solution.
The solution was transferred to a 2 litre Erlenmeyer flask partially filled with copper strips and fitted with a two hole rubber bung, through which a glass tube extended nearly to the bottom of the flask, and a second glass tube extended just into the neck of the flask. A stream of nitrogen was bubbled into the solution for a few minutes, and the solution was then allowed to stand, with occasional agitation, until it became clear.

(iii) Preparation of the apparatus.

A stream of nitrogen was blown through the absorption vessel $E$, to expel atmospheric oxygen, and the vessel was just over half filled with the acid cuprous chloride solution. A little liquid paraffin was poured into the open limb of the vessel to prevent the surface of the solution from coming into contact with the air. The vessel was then connected to the apparatus, and the liquid in the closed limb was drawn up to the level of tap 5. The absorption vessel $F$ was just over half filled with bromine solution, and this vessel was fixed to the apparatus, and the liquid drawn up to the level of tap 6. The absorption vessel $G$ was just over half filled with water, and the vessel was connected to the apparatus. Tap 7 was turned to position 1 (Figure 19), and the water in the closed limb of $G$ was drawn up to the level of tap 7. At the same time, water was drawn in through the sintered disc and
up the capillary tube until the levels of the water in both the capillary arms of tap 7 reached the barrel of the tap.

The vessel J was half filled with acetone and attached to the apparatus. The level of the liquid in the closed limb was then drawn up to tap 8. The apparatus was tested for leaks as described on page 30. Vessel A was evacuated, the burette C and the tubing between taps 3 and 4 were filled with mercury, and the apparatus was ready for use.

(iv) Procedure for operation of the apparatus.

1. Testing for carbon monoxide:—The cuprous chloride solution in vessel E was first drawn over to the barrel of tap 4, so that initially the connecting tubing between C and E was filled with the reagent. A sample of the non-condensible gas was drawn into A, and a portion of approximately 20 ml. was transferred to the burette C, and its volume noted. The gas was transferred to the absorption vessel E, and was allowed to remain in the vessel for roughly 10 seconds. It was then withdrawn to the burette and its volume measured. The process was repeated until no further change in volume occurred. The total decrease in volume was equal to the volume of carbon monoxide initially present.

2. Testing for unsaturation:—Two different unsaturation tests were performed. In one test, the gas was treated with bromine solution in the following manner.
The tubing between taps 4 and 8 was filled with dilute potassium bromide solution, drawn in from the boiling tube. A little of this solution was allowed to enter the burette. This portion served to prevent the formation of a thick scum in the burette, by dissolving any mercuric bromide formed on the surface of the mercury.

The sample of gas was drawn into the burette, and its volume measured. The gas was transferred to the vessel F containing the bromine solution, and after 2 minutes was withdrawn to the burette. The gas was then freed from bromine vapour by bubbling it through the water in the absorption vessel G. Tap 7 was turned to position 2 (Figure 19), and the gas was passed down the long capillary arm of tap 7 and through the sintered disc into the water. Tap 7 was turned to position 1, and the gas was withdrawn to the burette, and its volume measured. The unsaturation of the sample was indicated by a reduction in volume, and finally, complete absorption of the gas in the bromine solution, on repetition of the above operation.

It was usually necessary to leave the gas in the absorption vessel F for a considerable time to obtain complete absorption, as the addition reaction between perfluoro-olefines and bromine was seen to be very slow, and to have an appreciable induction period.
The second unsaturation test was carried out using a recently reported method (5). The gas was dissolved in acetone, and the solution was titrated against a solution of potassium permanganate in acetone. The test was performed as follows.

The tubing between taps 4 and 8 was filled with acetone from the vessel J. A sample of the gas to be examined was transferred to the burette, and its volume measured. Sufficient acetone was then drawn from the vessel J into the burette to dissolve completely the sample of gas in the burette. The acetone solution was expelled from the apparatus through tap 9 into a small beaker placed under the exit tube, and was titrated against a solution of potassium permanganate in acetone. The potassium permanganate solution, which was standardized against a solution of tetrafluoroethylene in acetone, was prepared so that 1 ml. of the solution was just sufficient to oxidize a solution of 1 ml. of tetrafluoroethylene in 10 ml. of acetone.
3. RESULTS.

(a) The examination of the gases present in the cylinder of tetrafluoroethylene.

A blank run was carried out with the furnace at room temperature. Six litres of gas were passed through the flow system and collected in the usual manner.

Approximately 60 ml. of non-condensible gas were collected in the charcoal trap. The molecular weight of this gas was determined by the gas density method, and a value of $29.1 \pm 1.5$ was obtained. A portion of the gas was transferred to the gas analysis apparatus and treated with acid cuprous chloride solution. No gas was absorbed. It was therefore concluded that this non-condensible gas was nitrogen.

The condensible gas was distilled in the large distilling column and found to contain 95% of tetrafluoroethylene, b.p.t. $-76^\circ C.$, together with 5% of a mixture of impurities which boiled at temperatures between $-90^\circ$ and $-84^\circ C$. This mixture of low boiling impurities was separated from the bulk of the tetrafluoroethylene by fractional distillation, and it was then redistilled in the small column. Approximately 50% of this mixture of impurities boiled over the temperature range $-90^\circ$ to $-87.5^\circ C.$, and the remainder boiled at $-84^\circ C$. A rough separation of these two components was made by a further fractional distillation.
The portion boiling at -84°C. was found to have a molecular weight of approximately 40, and to be readily soluble in water. On adding a little silver nitrate solution to an aqueous solution of the gas, a white precipitate was formed which redissolved in ammonia. The gas was therefore concluded to be hydrogen chloride (b.p.t. -83.7°C.; mol.wt. 36.5). This conclusion was supported by the results of a series of rough vapour pressure measurements carried out on a portion of the gas. These results were found to agree, within the limits of experimental error, with those given in the literature for hydrogen chloride.

The portion of the impurities boiling over the range -90° to -87.5°C. was found to have a molecular weight of approximately 78. Roughly half of this gas was found to dissolve readily in water. Of the remaining gas, approximately 50% was absorbed slowly in a strong solution of bromine in potassium bromide. This variable boiling point portion of the impurities was therefore concluded to contain a mixture of fluorinated ethanes and ethylenes together with hydrogen chloride.

The analysis of the gases in the cylinder was therefore as follows: tetrafluoroethylene, 94%; hydrogen chloride, 3.5%; nitrogen, 1%; fluorinated ethanes and ethylenes, 1.5%.

In all the runs described below, the condensible
products of pyrolysis were found to contain a volume of low boiling impurities equal to 3% of the tetrafluoroethylene pyrolysed. As will be shown later, these impurities had no effect on the nature or the amount of the products of pyrolysis of tetrafluoroethylene at 500°C and 700°C. The decrease in the percentage of low boiling impurities obtained in the flow runs as compared with that obtained in the blank run, was probably due to the fact that when the blank run was carried out, the rate at which the gas passed through the flow system was much faster than that used in the actual flow experiments. Hence, a larger proportion of the hydrogen chloride may have been absorbed in the water in the indicating wash-bottle.

(b) The products of pyrolysis of tetrafluoroethylene.

The thermal decomposition of tetrafluoroethylene was investigated over the temperature range 300°C to 700°C, using the silica reaction vessel, and over the range 400°C to 800°C, using the steel vessel. About 1 litre of tetrafluoroethylene was passed in each run. The pressure in the reaction vessel was maintained at 1 atmosphere during the pyrolysis by adjustment of the tap between the reaction vessel and the collecting traps and also the cylinder valve.

The condensible products of pyrolysis were analysed by fractional distillation in the small column. The results obtained are shown in Table 4. The distillation curves obtained
FIGURE 2O
DISTILLATION OF PRODUCTS OF PYROLYSIS OF TETRAFLUOROETHYLENE AT 400°C IN STEEL VESSEL

FIGURE 21.
DISTILLATION OF PRODUCTS OF PYROLYSIS OF TETRAFLUOROETHYLENE AT 600°C IN STEEL VESSEL
**Figure 22**

**DISTILLATION OF PRODUCTS OF PYROLYSIS OF TETRAFLUOROETHYLENE AT 700°C. IN STEEL VESSEL**

**Figure 23**

**DISTILLATION OF PRODUCTS OF PYROLYSIS OF TETRAFLUOROETHYLENE AT 800°C. IN STEEL VESSEL.**
Table 4.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Reaction Vessel</th>
<th>C₂F₄ passed ml. per min.</th>
<th>CF₄</th>
<th>C₂F₄</th>
<th>C₂F₆</th>
<th>C₃F₆</th>
<th>C₄F₈ cyclic</th>
<th>C₄F₈ b.pt. to +4.5°C</th>
<th>C₄F₈ b.pt. +6°C</th>
<th>liquids</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>silica</td>
<td>19.3</td>
<td>-</td>
<td>94.6</td>
<td>-</td>
<td>-</td>
<td>2.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>400</td>
<td></td>
<td>23.2</td>
<td>-</td>
<td>59.2</td>
<td>-</td>
<td>-</td>
<td>20.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>500</td>
<td></td>
<td>19.4</td>
<td>-</td>
<td>13.5</td>
<td>-</td>
<td>-</td>
<td>43.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>600</td>
<td></td>
<td>18.6</td>
<td>-</td>
<td>2.4</td>
<td>-</td>
<td>5.2</td>
<td>41.7</td>
<td>approx. 0.1ml. liquid</td>
<td>b.pt. &gt; -5.5°C.</td>
<td>-</td>
</tr>
<tr>
<td>700</td>
<td></td>
<td>19.0</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>carbon monoxide and silicon tetrafluoride formed.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>steel</td>
<td>59.2</td>
<td>-</td>
<td>59.5</td>
<td>-</td>
<td>-</td>
<td>20.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>600</td>
<td></td>
<td>66.7</td>
<td>-</td>
<td>5.6</td>
<td>-</td>
<td>4.6</td>
<td>39.5</td>
<td>approx. 0.1ml. liquid</td>
<td>b.pt. &gt; -5.5°C.</td>
<td>-</td>
</tr>
<tr>
<td>700</td>
<td></td>
<td>60.5</td>
<td>-</td>
<td></td>
<td></td>
<td>20.5</td>
<td></td>
<td>9.4</td>
<td>21.8</td>
<td>2.9</td>
</tr>
<tr>
<td>800</td>
<td></td>
<td>62.4</td>
<td>trace</td>
<td>25.0</td>
<td>2.1</td>
<td></td>
<td></td>
<td>-</td>
<td>16.7</td>
<td>2.5</td>
</tr>
</tbody>
</table>

*Also a tarry liquid condensed in exit tube of reaction vessel.

*Per litre of tetrafluoroethylene passed.
from the analysis of the condensible products formed in the runs carried out at 400°, 600°, 700°, and 800°C., using the steel reaction vessel, are shown in Figures 20, 21, 22, and 23.

Small amounts of white polymer dust were deposited in the exit tube of the reaction vessel during pyrolysis at 500° and 600°C. At 800°C. a trace of carbon was deposited on the walls of the reaction vessel. The liquid products obtained at 800°C. were yellow in colour, and were therefore concluded to be highly unsaturated.

In the runs carried out at 700°C. using the silica vessel, the volume of non-condensible gas collected in the charcoal trap was approximately 30% of the tetrafluoroethylene passed instead of the usual 1%. A molecular weight determination was carried out on a sample of this gas by the gas density method, and a value of 27.1 ± 1.0 was obtained.

A portion of this gas was transferred to the gas analysis apparatus and treated with acid cuprous chloride solution. The gas was almost completely absorbed, and no colouration of the reagent occurred. It was therefore concluded that the non-condensible gas contained a large proportion of carbon monoxide. In all the other runs the non-condensible gas was entirely nitrogen.

The condensible products of pyrolysis from the run carried out at 700°C. using the silica vessel, could not be
distilled, as vigorous bumping occurred on heating the products in the distilling column bulb. They were therefore condensed out into a small tube and removed from the apparatus. These products were found to fume readily when allowed to warm in the air. On placing a small bead of water in the fumes, the bead became turbid. It was therefore concluded that the condensible products contained appreciable quantities of silicon tetrafluoride.

(c) The properties of the products of pyrolysis of tetrafluoroethene.

The physical and chemical properties of the products of pyrolysis were investigated for two purposes; to identify the compounds formed, by comparison with published properties, and to determine values for physical properties and ascertain chemical properties in instances where no data had hitherto been published.

Each fraction from the distilling column was further purified by fractionation between traps, a middle fraction being used for the investigation of the properties of the compound.

(1) Hexafluoroethene.

This compound was obtained in good yield from the pyrolysis of tetrafluoroethene at 800°C. It boiled at -79°C in the distilling column.
FIGURE 24.

VAPOUR PRESSURE OF HEXAFLUOROETHANE

- EXPERIMENTAL RESULTS.
- VALUES OF KUFF AND BRETSCHAIDER.
- VALUES OF PACE AND ASTON.
A molecular weight determination was carried out on a portion of the purified sample, and a value of 137.1 ± 1.0 was obtained. (Calc. 138.0)

The vapour pressure of hexafluoroethane was investigated over the temperature range -133° to -88° C. A graph of $\log_{10} P_{mm}$ against $1/T$ was plotted, and the points were found to lie on two curves intersecting at -100.6° C. (Figure 24). The graphs of $\log_{10} P_{mm}$ against $1/T$ plotted from the data given by Ruff and Bretschneider (42) and by Pace and Aston (43) are also shown.

There is close agreement between the three curves of $\log_{10} P_{mm}$ against $1/T$ for hexafluoroethane in the liquid state. The equation given by Pace and Aston, however, for the vapour pressure of solid hexafluoroethane is seen to give a curve which differs appreciably from those obtained from the results of Ruff and Bretschneider, and from the results obtained in this work. As was pointed out on page 47, the two curves obtained from the equations of Pace and Aston for the vapour pressure of hexafluoroethane in the liquid and solid states, indicate that the vapour pressure of the metastable state is less than that of the stable state. As this is impossible, it can only be concluded that the equation given by Pace and Aston for the vapour pressure in the solid state must be incorrect.
The graph of $\log_{10} P_{mm}$ against $1/T$ gives the following physical constants for hexafluoroethane,

- Melting point, $-100.6 \pm 1.0^\circ C$.
- Boiling point, $-77.5 \pm 1.0^\circ C$.

Vapour pressure of the liquid, $\log_{10} P_{mm} = 7.166 - \frac{845}{T}$

Latent heat of vaporization, $3870$ cal. per mole.

Trouton's constant, $19.7$.

The corresponding figures obtained by Ruff and Bretschneider, and by Pace and Aston, are given on pages 46 and 47.

(ii) Hexafluoropropene.

Small yields of this compound were obtained from the pyrolysis of tetrafluoroethylene at $600^\circ$ and $800^\circ$C. and it was obtained in good yield from the products of pyrolysis at $700^\circ$C. The three samples boiled at $-30 \pm 1^\circ C$ in the distilling column. The samples from the pyrolysis at $600^\circ$ and $700^\circ$C. were found to have the same physical properties, and were both identified as hexafluoropropene. The sample obtained from the pyrolysis at $800^\circ$C. was too small to permit its separation and identification, but it was concluded to be hexafluoropropene on the basis of its similar boiling point in the distilling column.

Molecular weight determinations were carried out on purified portions of the samples of hexafluoropropene obtained from pyrolysis of tetrafluoroethylene at $600^\circ$ and $700^\circ$C.
Values of $150.0 \pm 0.6$ and $150.1 \pm 0.6$ were obtained. (calc 150.0)

The vapour pressure of liquid hexafluoropropene was measured over the temperature range $-89^\circ$ to $-44^\circ$C. The results obtained are given in Table 5. A graph of $\log_{10}P_{\text{mm}}$ against $1/T$ was plotted, and the points were found to lie on a straight line.

Table 5.

<table>
<thead>
<tr>
<th>Temp. (^\circ)C</th>
<th>Vapour pressure (\text{mm.})</th>
<th>Temp. (^\circ)C</th>
<th>Vapour pressure (\text{mm.})</th>
</tr>
</thead>
<tbody>
<tr>
<td>-88.6</td>
<td>19.5</td>
<td>-69.3</td>
<td>84</td>
</tr>
<tr>
<td>-83.2</td>
<td>30</td>
<td>-65.0</td>
<td>111.5</td>
</tr>
<tr>
<td>-79.2</td>
<td>41</td>
<td>-55.7</td>
<td>193</td>
</tr>
<tr>
<td>-74.8</td>
<td>56</td>
<td>-44.2</td>
<td>380</td>
</tr>
</tbody>
</table>

The physical properties of hexafluoropropene are as follows,

- melting point (by observation), $-155^\circ \pm 5^\circ$C.
- boiling point (by extrapolation), $-30.2 \pm 1^\circ$C.
- vapour pressure of liquid, $\log_{10}P_{\text{mm.}} = 7.908 - \frac{1221}{T}$.
- latent heat of vaporization, 5589 cal. per mole.
- Trouton's constant 23.0.

The melting and boiling points agree, within the limits of experimental error, with those given by Henne and
Waelkes (76).

A portion of the gas was transferred to the gas analysis apparatus and treated with bromine water. The gas was very slowly absorbed at first, but after a few seconds there was a rapid increase in the rate of absorption. The addition reaction between bromine and hexafluoropropene appeared to take place at the walls of the absorption vessel, and continued until no gas remained in the vessel.

Approximately 10 ml. of the gas were dissolved in acetone and the solution was titrated against a dilute solution of potassium permanganate in acetone. The solution of hexafluoropropene decolourized the same volume of potassium permanganate solution as was decolourized by a solution of 10 ml. of tetrafluoroethylene in acetone. This indicated that the gas consisted of an unsaturated compound containing one double bond.

(iii) Octafluorocyclobutane.

This compound is the principal product of pyrolysis of tetrafluoroethylene at 600°C. and below. It boiled at -5.5°C. in the distilling column.

A molecular weight determination was carried out on a portion of the gas used to determine accurate kinetic data (see page 152) and purified as described on page 136. A value of 200.3 ± 0.8 was obtained. (Calc. 200.0)
Figure 25

VAPOR PRESSURE OF OCTAFLUOROCYCLOBUTANE.
The vapour pressure of octafluorocyclobutane was measured at temperatures over the range \(-70^\circ\) to \(-10^\circ\)C. A graph of \(\log_{10} p_{\text{mm}}\) against \(1/T\) was plotted, and the points were found to lie on two straight lines intersecting at \(-38.7^\circ\)C. (Figure 25).

The physical properties of octafluorocyclobutane are as follows,

- Melting point \(-38.7 \pm 0.5^\circ\)C.
- Boiling point (by extrapolation), \(-5.5 \pm 0.5^\circ\)C.
- Vapour pressure of solid, \(\log_{10} p_{\text{mm}} = 8.937 - 1580/T\)
- Vapour pressure of liquid, \(\log_{10} p_{\text{mm}} = 7.724 - 1295/T\)
- Latent heat of vaporization, 5928 cal. per mole.
- Trouton's constant, 22.2

On treatment of a solution of the gas in acetone with potassium permanganate solution, no decolourization was observed, indicating that the compound was saturated.

(iv) The octafluorobutenes.

The products of pyrolysis of tetrafluoroethylene at 700\(^\circ\)C. contained a portion boiling over the range \(-1^\circ\) to \(+4.5^\circ\)C. This variable boiling point fraction was split up by further distillation into two portions which boiled over the ranges \(-1^\circ\)C. to \(+1.5^\circ\)C. and \(2^\circ\)C. to \(4.5^\circ\)C. Molecular weight determinations were carried out on these two portions, and values of 202.4 and 202.6 were obtained. (calc. 200.0)
10 ml. of each portion were transferred to the gas analysis apparatus and dissolved in acetone. The solutions were titrated with potassium permanganate solution standardized against a solution of tetrafluoroethylene in acetone. The results indicated that both portions of the gas contained only an unsaturated compound with one double bond. It was therefore concluded that the variable boiling point portion contained a mixture of cis and trans octafluorobutene-2, as described by Henne and Newby (82).

No absorption was observed when the gas was treated with bromine water, although octafluorobutene-2 has been reported to react with bromine (5). The reaction occurred under much more vigorous conditions, however, than those employed in the gas analysis apparatus (see page 74).

Attempts to react the gas with hydrogen bromide in the presence of an activated carbon-calcium sulphate catalyst at 100°C. were inconclusive. The catalyst was similar to that recommended by Park, Sharrah and Lacher (62), for the addition of hydrogen bromide to tetrafluoroethylene and hexafluoropropene.

The two samples boiling at 6°C, obtained from the pyrolysis of tetrafluoroethylene at 700°C and 800°C, were found to have identical properties, and were concluded on the basis of earlier results (5) to be octafluorobutene-1.
Molecular weight determinations were carried out on purified portions of the two samples, and values of 199.8 ± 1.0 and 200.4 ± 1.0 were obtained.

The vapour pressure of the liquid was determined over the range -70° to -13°C. The results obtained are given in Table 6. A graph of log10Pmm. against 1/T was plotted, and the points were found to lie on a straight line.

Table 6.
The vapour pressure of octafluorobutene-1.

<table>
<thead>
<tr>
<th>Temp. °C.</th>
<th>Vapour pressure mm.</th>
<th>Temp. °C.</th>
<th>Vapour pressure mm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>-69.7</td>
<td>8</td>
<td>-38.2</td>
<td>77</td>
</tr>
<tr>
<td>-64.7</td>
<td>12</td>
<td>-31.0</td>
<td>124</td>
</tr>
<tr>
<td>-54.8</td>
<td>25.5</td>
<td>-23.0</td>
<td>191</td>
</tr>
<tr>
<td>-46.0</td>
<td>47</td>
<td>-13.6</td>
<td>314</td>
</tr>
</tbody>
</table>

The physical properties of octafluorobutene-1 are as follows,

melting point (by observation), -118° ± 5°C.
boiling point (by extrapolation), 5.7° ± 0.5°C.
vapour pressure of liquid, log10Pmm. = 8.316 - 1508/T.
latent heat of vaporization, 6901 cal. per mole.
Trouton's constant, 24.7

An unsaturation test was performed by titrating a solution of the gas in acetone with standard potassium
permanganate solution. The result showed that the gas consisted of an unsaturated compound with one double bond. The gas was not absorbed in bromine water, and did not react with hydrogen bromide in the presence of a carbon-calcium sulphate catalyst.

(v) The pyrolysis of pure tetrafluoroethylene.

A series of experiments were carried out to determine the effect of the impurities present in the tetrafluoroethylene used in the flow runs on the nature and yield of the products formed. The apparatus used was as shown in Figure 27, and described on page 131.

Approximately 2 litres of tetrafluoroethylene were purified by fractional distillation. Samples of the pure gas were heated for approximately 1 minute at 500°C, using a Pyrex reaction vessel, and for the same time at 700°C, using a steel reaction vessel. The products formed by pyrolysis of 1 litre of gas at each temperature were collected and analysed by fractional distillation. The results obtained are given in Table 7, and the distillation curve for the products of pyrolysis at 700°C, is shown in Figure 26.

The products formed by pyrolysis of the pure gas are seen to be identical with those obtained from the pyrolysis of the impure gas at the same temperatures. The yields of the various products are similar, although the products of pyrolysis of the pure gas at 700°C, contain more hexafluoro-
propene and less octafluorobutene-1 than obtained from the pyrolysis of the impure gas. This slight difference in the yields may be attributed to the different reaction times employed in the two experiments. The exact reaction time in the flow run at 700°C. is uncertain, but it was probably less than one minute. It was, therefore, concluded that the impurities present in the tetrafluoroethylene used in the flow experiments had no appreciable effect on any of the reactions occurring.

Table 7.
The products of pyrolysis of pure tetrafluoroethylene.

<table>
<thead>
<tr>
<th>Temp °C.</th>
<th>PRODUCTS g. mol. per 100 g. mol. pyrolysed.</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C₂F₄</td>
<td>C₃F₅</td>
</tr>
<tr>
<td>500</td>
<td>15.5</td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>1.4</td>
<td>31.0</td>
</tr>
</tbody>
</table>

(vi) The infra-red spectra of the products of pyrolysis of tetrafluoroethylene.

Dr. Minkoff of the Chemical Technology Department, Imperial College, very kindly agreed to examine the infra-red spectra of the fluorocarbons formed by the pyrolysis of tetrafluoroethylene.

This examination was carried out principally with a view to obtaining further evidence on the nature of the
Figure 2.6

Distillation of products of pyrolysis of pure tetrafluoroethylene at 700°C in steel reaction vessel.
variable boiling point product formed by the pyrolysis of tetrafluoroethylene at 700°C. Four samples were taken from the products of pyrolysis at 700°C, as shown in Figure 26. Each sample was further purified by fractionation between traps. The infra-red spectra of these purified samples were examined, and also that of a sample of octafluorocyclobutane, purified by fractional distillation.

The following observations were made:

All the lines found in the spectrum of octafluorocyclobutane corresponded to those given in published data. The sample was therefore concluded to be free from impurities.

The spectrum of Sample 1 indicated that in addition to hexafluoropropene, this sample contained a small amount (probably less than 1%) of octafluorocyclobutane.

Certain strong lines in the spectrum of octafluorocyclobutane were not observed in the spectra of Samples 2, 3, and 4. It was therefore concluded that these samples contained no octafluorocyclobutane. It was also observed that Sample 2 contained no hexafluoropropene.

All the spectra, except that of octafluorocyclobutane, contained lines which indicated the presence of a compound containing a double bond.

By comparison of the spectra of Samples 2, 3, and 4, it appeared that Sample 2 contained 96 to 99% of a substance A
together with 1 to 4% of a substance B, whilst Sample 3 consisted of a mixture of A and B in the approximate ratio 4 parts of A to 1 part of B. Sample 4 appeared to contain approximately 96% of B together with roughly 4% of A.

These observations are in accordance with the theory that the variable boiling point product consisted of a mixture of cis and trans octafluorobutene-2, and that the compound boiling at 60°C. was octafluorobutene-1. It appears, however, that the variable boiling point mixture also contained an appreciable amount of octafluorobutene-1.

(d) Summary.

The thermal decomposition of tetrafluoroethylene has been investigated by the flow method, over the temperature range 300° to 800°C. Below 600°C. the only product obtained in measurable yield is octafluorocyclobutane. At 600°C. and above, unsaturated products such as hexafluoropropene and octafluorobutenes are formed. At 800°C. the saturated fluorocarbon, hexafluoroethane is formed in large yield, A trace of carbon tetrafluoride is also formed at this temperature.

The physical and chemical properties of the products of pyrolysis of tetrafluoroethylene have been examined. The determinations of the vapour pressures of hexafluoropropene, octafluorocyclobutane, and octafluorobutene-1 are reported. No vapour pressure data for these compounds have been found
in the literature.

Hexafluoropropene is absorbed in bromine water, although the initial rate of absorption is very slow. The addition reaction between bromine and hexafluoropropene appears to take place at the walls of the reaction vessel, and thus resembles the reaction between bromine and tetrafluoroethylene (1). By contrast, the octafluorobutenes are quite unreactive towards bromine water, and also towards hydrogen bromide in the presence of a carbon–calcium sulphate catalyst. These results suggest that the inductive effect of a CF₃ group attached to a carbon atom adjacent to a double bond, which causes deactivation of the double bond towards electrophilic reagents, is much greater than that of a fluorine atom in a similar position.

The results obtained from the investigation of the thermal decomposition of tetrafluoroethylene are discussed in Part IV of this thesis.
PART III: THE INVESTIGATION OF THE KINETICS OF THE

REACTION $2\text{C}_2\text{F}_4 \rightleftharpoons \text{C}_4\text{F}_8$ (cyclic)

1. INTRODUCTION.

The results obtained from the investigation of the thermal reactions of tetrafluoroethylene using the flow method indicate that below 600°C, the principal reaction occurring is the dimerization of tetrafluoroethylene to give octafluorocyclobutane,

$$2\text{C}_2\text{F}_4 = \text{C}_4\text{F}_8 \text{ (cyclic)} \quad (1)$$

This section gives details of a series of experiments performed to obtain accurate kinetic data for this reaction. It was found that at temperatures above 500°C, the reverse reaction

$$\text{C}_4\text{F}_8 \text{ (cyclic)} = 2 \text{C}_2\text{F}_4 \quad (2)$$

occurs at a measurable rate. The kinetics of this reaction have also been studied.
Plate 4. The Static Type Apparatus.
**Figure 2.7**

THE STATIC TYPE APPARATUS

**Figure 27**

**Figure 28**

DETAILS OF METAL-GLASS JOINT.
2. EXPERIMENTAL.

(a) Method.

In the investigation of the dimerization of tetrafluoroethylene, samples of gas were heated in a closed vessel at a series of temperatures between 300° and 550°C. The pressure inside the reaction vessel was measured at various times and the rate of reaction was determined from the results obtained. The thermal decomposition of octafluorocyclobutane was studied over the temperature range 520° to 590°C by a similar method.

(b) Apparatus.

The apparatus used for the investigation of the dimerization of tetrafluoroethylene over the temperature range 300° to 550°C. and the decomposition of octafluorocyclobutane over the range 520° to 550°C is shown in Figure 27, and in Plate 4. The apparatus was constructed of soda-glass except for the Pyrex reaction vessel E. The details of this vessel are shown in Figure 29.

The vessel C of approximately 750 ml. capacity, which was used as a gas reservoir, was connected through the tap F to the vacuum pump, and also to the gas supply. It was also connected to one arm of the 1 mm. bore double-oblique vacuum tap D.

The reaction vessel E was connected to the arm on the
**Figure 29** Details of Pyrex Reaction Vessel

**Figure 29a** Details of Steel Reaction Vessel
opposite side of tap D by means of 1 mm. bore capillary tubing. This connecting tubing was made as short as possible so as to minimise the dead space between tap D and the tubing in the furnace. The manometer B was also of 1 mm. bore capillary tubing. The reaction vessel was attached at M by means of a tapered joint sealed with picein. The third arm of tap D was connected to the vacuum pump and collecting traps as shown.

In the investigation of the thermal decomposition of octafluorocyclobutane at temperatures above 550°C., the Pyrex reaction vessel was replaced by a steel vessel, the details of which are shown in Figure 29a. The end of the capillary tube from the steel vessel was fitted into a glass sleeve, which replaced the joint at M. The end of the sleeve was sealed to the metal tube with picein. This picein seal was kept cool by means of a water jacket as shown in Figure 28.

Before use, the inside of the steel vessel was freed from oxide scale by heating the vessel to 700°C. and passing a steady stream of hydrogen through the vessel for several hours. The end of the small tube X (Figure 29a) was then sealed by welding.

The pressure inside the reaction vessel was read on the barometric manometer B, which was calibrated in the following manner. The reaction vessel was filled with air to a pressure
just below 1 atmosphere and the levels of the mercury in the two limbs of the manometer were noted. The pressure inside the vessel was then reduced slightly and the mercury levels were again read. This process was repeated until all the air had been removed from the reaction vessel. Before all mercury level readings were taken the manometer was tapped gently to obviate any errors due to sticking of the mercury. A graph of pressure inside the reaction vessel against height of mercury in the right hand limb of the manometer was plotted from the series of values obtained. In practice, the level of the mercury in the right hand limb of the manometer was noted, and the pressure inside the reaction vessel was obtained from the calibration graph.

When investigating the dimerization of tetrafluoroethylene, the mercury levels were read to the nearest $\frac{1}{2}$ mm. by means of a scale placed behind the manometer. In the investigation of the decomposition of octafluorocyclobutane, more accurate pressure readings were necessary, as the rate of change of pressure and the total pressure change were much less than in the tetrafluoroethylene reaction. It was found possible to follow the change in the level of the mercury during the decomposition reaction by means of a cathetometer. Readings of the levels were thereby obtained to $\pm \ 0.1 \ mm$.

The Pyrex and steel reaction vessels were heated in a
horizontal, wire-wound, tubular furnace. This was constructed by winding a coil of approximately 140 turns of 22 S.W.G. nichrome wire, of 2.54 ohms resistance per yard, onto a Mullite tube 2 feet in length and of internal diameter 2 inches, and ½ inch thickness. The coil was wound to cover 17½ inches of the length of the tube, equal spaces being left uncovered at each end. The total resistance of the coil was 80 ohms. The methods of winding and packing of the tube were similar to those described on pages 86 to 88. The same Syndenyo box was used for both furnaces, and as before, the heating coil was connected to the 230 volt a.c. mains through a Sunvic Energy Regulator.

The Pyrex reaction vessel was packed into the furnace tube with asbestos string and wool as shown in Figure 27, and the steel vessel was packed in a similar manner. The temperature inside each vessel was measured by means of a chromel-alumel thermocouple in conjunction with a Doran potentiometer. The "hot" junction was placed inside the thermocouple well of the reaction vessel. The thermocouple, which was constructed as described on page 101, was standardized against a platinum-platinum/rhodium thermocouple, and found to be correct to within less than 1°C. over the experimental temperature range.

The uniformity of the temperature inside each of the reaction vessels was checked with the furnace at a steady
temperature within the experimental temperature range. The temperature along the length of the Pyrex vessel was made uniform to within ±0.5°C. by winding a suitable number of layers of asbestos string around the ends of the furnace tube which protruded beyond the ends of the Syndano box. For the steel vessel, the temperature along its length was made uniform to within ±1°C. by adding further layers of asbestos string and covering this with a thick layer of glass wool, bound on with copper wire.

(c) The materials used.

The tetrafluoroethylene used in the experiments described below was taken from a cylinder of the gas (see page 84). Five-litre samples of the gas were transferred to the apparatus as required and were purified by fractional distillation in the large column. In these distillations, the column was made semi-automatic by using the device described on page 97. The first litre of distillate was collected in bulb A (Figure 9), the next three litres were collected in bulb B, and the undistilled portion remaining in the distilling column was then transferred to bulb A. The middle portion of the distillate, collected in bulb B, was used in the experiments described below.

The vapour pressure of the purified gas was measured over the temperature range -110°C to -87°C. A graph of log_{10}P vs.
Figure 30

VAPOR PRESSURE OF TETRAFLUOROETHYLENE

- O - EXPERIMENTAL RESULTS
- △ - VALUES OF RUFF
against 1/T was plotted, and the points were found to lie on a straight line (Figure 30) giving

\[ \log_{10} P_{\text{mm}} = 7.686 - 944.2/T \]

boiling point (by extrapolation) \(-76.5 \pm 0.4^\circ C\).

(Ruff and Bretschneider give b.pt. \(-76.3^\circ C\).)

It is seen from Figure 30 that the results are in excellent agreement with those calculated from the equation given by Ruff and Bretschneider (42).

Molecular weight determinations by the vapour density method were performed on samples of the purified gas, and values of \(99.7 \pm 0.4\) and \(100.0 \pm 0.4\) were obtained (calculated value \(100.0\)).

Pure octafluorocyclobutane was obtained by pyrolysis of tetrafluoroethylene in the flow system at \(600^\circ C\), and subsequent fractional distillation of the products of pyrolysis. Eight-litre samples of the gas were pyrolysed using the steel reaction vessel, and the products of pyrolysis were collected in the normal manner and fractionated in the large distilling column using the semi-automatic device. The unchanged tetrafluoroethylene and the first 500 ml. of octafluorocyclobutane were collected in bulb A (Figure 9). The next 2½ litres of octafluorocyclobutane were collected in bulb B, and the final distillate was collected in bulb A. The portion of the distillate collected in bulb B was used in the experiments described below.
Molecular weight and vapour pressure determinations were carried out on samples of the purified gas. The results obtained are given on pages 121 and 122. An examination of the infra-red spectrum of a sample of this gas showed the gas to be free from impurities.

(d) Procedure for operation of the apparatus.

The furnace was switched on, and allowed 20 hours to reach the steady temperature required. After this time it was found that the temperature inside the reaction vessel remained constant to within ± 10°C, for periods of time up to approximately 15 minutes.

The whole apparatus was evacuated by pumping, and a volume of the gas to be pyrolysed was then transferred to bulb C (Figure 27). The temperature in the reaction vessel was noted, and the apparatus was ready for use.

Tap D was turned to connect the bulb C with the reaction vessel and was kept open for approximately 2 seconds. A stopwatch was started at the moment of closing tap D. The manometer B was tapped gently, and the mercury level in the right hand limb was read at intervals until the rate of change of pressure with time became very slow.

The reaction products were removed from the reaction vessel by turning taps D and H to connect the vessel with a collecting trap cooled in liquid nitrogen. The final traces of reaction product were removed by pumping.
3. RESULTS.

(a) The dimerization of tetrafluoroethylene.

The dimerization of tetrafluoroethylene was studied at a number of temperatures over the range 300° to 550° C, using the Pyrex reaction vessel. A series of six to eight runs were performed at each temperature, and values for the velocity constant of the dimerization reaction were calculated from the results obtained in each run.

The products of pyrolysis from the runs carried out at 500°, 525°, and 550° C. were collected and analysed by fractional distillation. They were found to contain only tetrafluoroethylene and octafluorocyclobutane. It was, therefore, concluded that the only reaction occurring at temperatures below 550° C. was the dimerization of tetrafluoroethylene to octafluorocyclobutane.

(i) The evaluation of \( P_0 \).

On closing tap D, the pressure in the section of the apparatus beyond tap D took 3 to 3½ seconds to come to equilibrium. It was not possible, therefore, to obtain a direct reading of the initial pressure, \( P_0 \), inside the reaction vessel.

In the runs carried out at 300° and 325° C. there was very little change in pressure during the first 20 seconds of the reaction. At these temperatures it was possible to estimate
reasonably accurately the value of $p_0$, by inspection of the figures obtained for the pressure in the reaction vessel after 5, 10, 15, and 20 seconds. Examples of the initial pressure readings obtained in runs performed at 300° and 325°C are shown in Table 8. The estimated values of $p_0$ are also given.

**Table 8.**

The pyrolysis of tetrafluoroethylene at 300°C.

<table>
<thead>
<tr>
<th>Time (seconds)</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure in reaction vessel (mm)</td>
<td>524</td>
<td>524</td>
<td>524</td>
<td>523</td>
</tr>
<tr>
<td>Estimated $p_0$, mm.</td>
<td>524</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time (seconds)</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure in reaction vessel (mm)</td>
<td>386</td>
<td>386</td>
<td>386</td>
<td>385</td>
</tr>
<tr>
<td>Estimated $p_0$, mm.</td>
<td>386</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The pyrolysis of tetrafluoroethylene at 325°C.

<table>
<thead>
<tr>
<th>Time (seconds)</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure in reaction vessel (mm)</td>
<td>375</td>
<td>374</td>
<td>374</td>
<td>373</td>
</tr>
<tr>
<td>Estimated $p_0$, mm.</td>
<td>375</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time (seconds)</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure in reaction vessel (mm)</td>
<td>396.0</td>
<td>395.5</td>
<td>395.5</td>
<td>394.0</td>
</tr>
<tr>
<td>Estimated $p_0$, mm.</td>
<td>396</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It was found necessary to calculate values for $p_0$ from the results obtained in runs performed at 350°C and above, since at these temperatures appreciable pressure changes occurred during the first 20 seconds of the reaction, and reliable values for $p_0$ could no longer be estimated from the pressure figures obtained during this period.

Assuming that during the first two minutes of pyrolysis the only reaction occurring is the simple dimerization

$$2C_2F_4 = C_4F_8$$
then the second order equation
\[ k = \frac{2(P_0 - P_t)}{P_0 t (2P_t - P_0)} \]  
should be obeyed, where \( P_0 \) represents the initial pressure inside the reaction vessel, and \( P_t \) the pressure after a time \( t \).

The above equation may be rearranged to the form
\[ 2(P_0 - P_t) = \frac{p_0^{2kt}}{1 + p_0^{kt}} \]  
An approximate value for \( k \) was obtained by extrapolation of a graph of \( \log_{10} k \) against \( 1/T \), plotted using the figures obtained for \( k \) from runs performed at lower temperatures. A rough figure for \( P_0 \) was obtained by inspection of the values for the pressure in the reaction vessel after 5, 10, 15, and 20 seconds. Using these rough values for \( k \) and \( P_0 \), a series of values for \( 2(P_0 - P_t) \) were calculated for different values of \( t \), by substitution into equation (2).

A value for \( P_0 \) was derived from each of the figures for \( 2(P_0 - P_t) \) obtained by the above method, by substituting the measured pressure values for \( P_t \). If these values for \( P_0 \) agreed with each other, and with the rough value originally assumed for \( P_0 \), to within 0.5 mm., then this rough value for \( P_0 \) was taken as the correct figure, and was used to calculate the velocity constant \( k \) by the method described below. If, however, a big discrepancy existed between the calculated figures for \( P_0 \) and the rough value, then a new value was assumed for \( P_0 \) and the calculations were repeated until agreement was obtained.
In a few instances, the value finally obtained for $k$ differed slightly from the rough value obtained by extrapolation of the graph of $\log_{10}p$ against $1/T$. In these cases, a fresh value for $k$ was taken and the calculation was repeated until the initial rough value and the final value were approximately the same. It was found, however, that a small change in the rough value for $k$ had little effect on the value finally calculated for $p_0$, and hence this recalculation was seldom necessary. The calculation of $p_0$ from the results obtained in a run performed at $350^\circ C$, is shown below as an example of the procedure adopted.

The pressure values obtained at various times during the first minute of the reaction are given in Table 9. From an inspection of the first four pressure figures given in the table, $p_0$ was concluded to be approximately $537.5$ mm. From the values obtained for the velocity constants at $300^\circ$ and $325^\circ C$, the magnitude of $k$ at $350^\circ C$, was seen to be approximately $3.3 \times 10^{-6} \text{ mm}^{-1} \text{ sec}^{-1}$.

The calculated values for $p_0$ given in Table 9 are seen to agree with each other and with the rough value assumed for $p_0$ to within less than $0.5$ mm., and hence the rough value of $537.5$ mm. was taken as the correct figure for $p_0$ within an accuracy of $\pm 0.5$ mm. This accuracy is satisfactory since the limits of experimental error are also $\pm 0.5$ mm.
Table 9.

Evaluation of \( p_0 \) for a run performed at 350° C.

<table>
<thead>
<tr>
<th>Rough value of ( p_0 )</th>
<th>537.5 mm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Approximate value of ( k )</td>
<td>( 3.3 \times 10^{-6} ) mm(^{-1}) sec(^{-1})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time (secs.)</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>40</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (mm.) ((p_t))</td>
<td>535</td>
<td>533</td>
<td>531</td>
<td>528.5</td>
<td>520</td>
<td>511.5</td>
</tr>
<tr>
<td>Calculated values of ((p_0-p_t))</td>
<td>9.2</td>
<td>17.9</td>
<td>26.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Derived values for ( p_0 )</td>
<td>537.7</td>
<td>537.9</td>
<td>537.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Taking the value of 537.5 mm. for \( p_0 \), \( k \) was found to be \( 3.43 \times 10^{-6} \) mm\(^{-1}\) sec\(^{-1}\). This result is close to the approximate value taken for \( k \), and hence recalculation of \( p_0 \) using a fresh value for \( k \) was not necessary. If the figure of \( 3.4 \times 10^{-6} \) is used for \( k \) instead of \( 3.3 \times 10^{-6} \), the values calculated for \( p_0 \) differ by approximately 0.2 mm. from those given in Table 9. This difference is negligible, being less than the experimental error.

(ii) The evaluation of the velocity constant.

The velocity constants of the dimerization reaction of tetrafluoroethylene were calculated by the method shown below in which a correction is made for the small volume of gas in the dead space outside the furnace.

Let the volume and temperature of the reaction vessel be \( V_1 \) and \( T_1 \) respectively, and let the volume and temperature
of the dead space be $V_2$ and $T_2$ respectively. If the reaction vessel contains initially $n$ moles of tetrafluoroethylene, then the dead space will contain initially $\frac{T_1V_2}{T_2V_1}$ moles of tetrafluoroethylene.

If $x$ moles of tetrafluoroethylene dimerize in a time $t$, then $\frac{1}{2}x$ moles of octafluorocyclobutane will be formed in this time. This reaction will cause a decrease in pressure inside the reaction vessel and hence a number of the moles of tetrafluoroethylene in the dead space will move into the reaction vessel during the time $t$. Let this number be $y$. After a time $t$, there will therefore be $n - \frac{1}{2}x + y$ moles of gas in the reaction vessel, and hence $\frac{T_1V_2}{T_2V_1} (n - \frac{1}{2}x + y)$ moles of gas in the dead space.

Now the number of moles in the dead space after a time $t$ will be equal to the number originally present less the number which have passed into the reaction vessel, i.e.

$$\frac{T_1V_2}{T_2V_1} (n - \frac{1}{2}x + y) = \frac{T_1V_2}{T_2V_1} n - y$$

hence

$$y = x(\frac{T_1}{2V_1} \cdot \frac{1}{\frac{T_2}{V_2} + \frac{T_1}{V_1}})$$

Let the term inside the brackets in equation (2) be equal to $b$, i.e.

$$b = \frac{T_1}{2V_1} \cdot \frac{1}{\frac{T_2}{V_2} + \frac{T_1}{V_1}}$$

then the number of moles of tetrafluoroethylene in the reaction vessel after a time $t$ will be $n - x + y$, i.e. $n - x + bx$.

Hence the concentration of tetrafluoroethylene in
the reaction vessel will be
\[ \frac{n - x + bx}{V_1} \]  
\tag{4}

Assuming that the dimerization reaction obeys the second order equation, the rate of dimerization of tetrafluoroethylene is given by
\[ \text{Rate} = \frac{dx}{V_1 dt} = k \left[ \frac{n - x(1-b)}{V_1} \right]^2 \]  
\tag{5}

On integration of this equation we have
\[ \frac{1}{(1-b)(n - x(1-b))} = \frac{kt}{V_1} + K \]  
\tag{6}

where K is the integration constant. When \( t=0, \ x=0 \) and therefore \( K = 1/(1-b)n \). Thus we have
\[ \frac{kt}{V_1} - \frac{1}{(1-b)(n - x(1-b))} = \frac{1}{(1-b)n} \]  
\tag{7}

Let the initial pressure in the reaction vessel be \( P_0 \) and the pressure after a time \( t \) be \( P_t \), then
\[ P_t = (n - \frac{1}{2}x + bx) \frac{RT_1}{V_1} \]
\[ = n \frac{RT_1}{V_1} - x(\frac{1}{2} - b) \frac{RT_1}{V_1} \]  
\tag{8}

Let \( \frac{RT_1}{V_1} x = P_x \), then equation (8) becomes
\[ P_t = P_0 - P_x (\frac{1}{2} - b) \]  
\tag{9}

Equation (9) can be rearranged to the form
\[ P_0 - P_x (1-b) = P_0 - (P_0 - P_t) \left\{ \frac{1-b}{\frac{1}{2} - b} \right\} \]  
\tag{10}

It will be seen that \( P_x \) is equal to the decrease in pressure of the tetrafluoroethylene in the reaction vessel due to the reaction of \( x \) molecules of the gas.
From equation (7) we have

\[ kt = \frac{1}{(1-b) \left[ \frac{n}{V_1} - \frac{k}{V_1} (1-b) \right]} - \frac{1}{(1-b) \frac{n}{V_1}} \]

\[ = \frac{1}{(1-b) \left[ \frac{P_0}{760RT_1} - \frac{P_x}{760RT_1} (1-b) \right]} - \frac{1}{(1-b) \frac{P_0}{760RT_1}} \quad (11) \]

where \( R \) is in litre-atm. degree\(^{-1} \) mole\(^{-1} \) units and pressures are in mm. It is seen from equation (11) that the reciprocal of the slope of the graph of \( t \), in seconds, against \( \frac{1}{(P_0 - P_x(1-b))} \), will be equal to \( k \frac{(1-b)}{760RT_1} \), i.e.

\[ k = \frac{1}{\text{slope}} \cdot \frac{760RT_1}{(1-b)} \quad (12) \]

where \( k \) will be in (mole/litre\(^{-1} \) sec\(^{-1} \) units.

A sample of tetrafluoroethylene was introduced into the reaction vessel, the furnace being at room temperature, and the pressure in the vessel was noted. The sample of gas was then transferred to the standard volume bulb and its volume measured accurately. The volume of the reaction vessel plus the dead space \((V_1 + V_2)\) was calculated from the results obtained. \( V_2 \) was calculated from the length and diameter of the capillary tubing between tap D and the furnace, and \( V_1 \) was obtained by difference.

Values for \( b \) were calculated by introducing the volume figures obtained for \( V_1 \) and \( V_2 \) into equation (3), \( T_1 \) and \( T_2 \) being taken as the temperature of the furnace and room respectively.
FIGURE 31

PYROLYSIS OF TETRAFLUOROETHYLENE

AT 400°C.
Values for \( P_0 - P_x (1-b) \) were calculated using equation (10), and the reciprocals of these values were plotted against the time, t. Values for the velocity constant were calculated by substituting the slopes of the graphs obtained into equation (12).

The following calculations, which are given as an example, were performed using the results obtained from the pyrolysis of tetrafluoroethylene at 400°C.

The volume of the reaction vessel was found to be 257.7 ml., and that of the dead space 0.45 ml. On substituting these values into equation (3), a value of 0.998 was obtained for \( 1-b \) when \( T_2 \) was equal to 293°C. Hence \( \frac{1-b}{P_0 - P_x (1-b)} = 2.004 \).

The results of the remaining calculations are given in Table 10, and a graph of \( \frac{1}{P_0 - P_x (1-b)} \) against \( t \), plotted from the results given in the table, is shown in Figure 31. The points lie on a good straight line, and from the slope of this line a value of 0.6128 (mole/litre)\(^{-1}\) sec\(^{-1}\) was obtained for \( k \).

It is seen from Table 10 that the correction applied for the dead space error is very small. If this error is neglected, then the pressure of tetrafluoroethylene in the reaction vessel after a time \( t \) is given by \( (2P_t - P_0) \). After 180 seconds this value differs from the corrected value by only 0.5 mm., and after 725 seconds by 0.75 mm. Graphs of
Table 10.
The pyrolysis of tetrafluoroethylene at 400°C.
Initial pressure ($P_o$) = 455mm.

<table>
<thead>
<tr>
<th>Time (secs.)</th>
<th>$P_t$ (mm)</th>
<th>$P_o$-$P_t$</th>
<th>$p_x$(1-b)</th>
<th>$P_o$-$p_x(1-b)$</th>
<th>$\frac{1}{P_o-p_x(1-b)} \times 10^4$</th>
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<td>178</td>
<td>356.71</td>
<td>98.3</td>
<td>101.70</td>
</tr>
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</table>
**Figure 32**

Pyrolysis of Tetrafluoroethylene

At 300°, 326°, 350°, and 375°C

**Figure 33**

Pyrolysis of Tetrafluoroethylene

At 400°, 426°, 450°, and 476°C
Figure 34

Pyrolysis of Tetrafluoroethylene

at 500°, 525° and 550°C

\[ \frac{1}{P_a - P_c(1-b)} \times 10^5 (\text{mm}^{-1}) \]
\[ \frac{1}{(2P_t - P_0)} \] against \( t \) plotted using the results obtained from the pyrolysis of tetrafluoroethylene at 300°C. gave curves which deviated slightly from a straight line at high values of \( t \). The initial slopes of these graphs were, however, similar to the slopes of the graphs obtained on plotting the corrected results. Similar graphs plotted using the uncorrected results obtained at higher temperatures deviated more markedly from a straight line.

The corrected results obtained from the runs performed at 450°C and below gave good straight line graphs as shown in Figures 32 and 33. The graphs obtained for higher temperatures are seen to deviate slightly from a straight line (Figures 33 and 34), the deviation being more marked the higher the temperature.

This deviation was considered to be due either to the fact that the dimerization reaction is reversible or that another reaction was occurring at a measurable rate at temperatures above 450°C. As was pointed out earlier, the analysis of the products of pyrolysis obtained from runs carried out over the temperature range 500°C to 550°C. showed that only tetrafluoroethylene and octafluorocyclobutene were present. Hence, reactions leading to the formation of other products cannot occur at these temperatures. On heating a sample of octafluorocyclobutane at 525°C, an increase in pressure was observed, and
the products of pyrolysis consisted of octafluorocyclobutane together with a small amount of tetrafluoroethylene. It was therefore concluded that the dimerization reaction of tetrafluoroethylene is reversible and that at temperatures above 450°C, the reverse reaction occurs at a sufficiently fast rate to effect the graph plotted for the forward reaction using the second order rate equation. Values for the velocity constant of the dimerization reaction at temperatures above 450°C were calculated using the initial slopes of the graphs of $\frac{1}{p_o - p_x(1-b)}$ against $t$.

It is seen from Figure 34 that the graph plotted from the results obtained at 550°C begins to deviate from a straight line after approximately 100 seconds. In one particular run at this temperature, $p_o$ was equal to 305 mm. and $p_t$ after 130 seconds was 163 mm. Hence, the partial pressures of tetrafluoroethylene and octafluorocyclobutane in the reaction vessel after 130 seconds were 21 mm. and 142 mm. respectively. The velocity constant of the dimerization reaction was found to be 3.66 x 10⁻⁴ mm⁻¹ sec⁻¹ at 550°C., and the velocity constant of the reverse reaction at this temperature (v. infra) was found to be 19.39 x 10⁻⁵ sec⁻¹. Thus after 130 seconds, the rate of change of the partial pressures of tetrafluoroethylene and octafluorocyclobutane were
\[
\frac{\mathrm{dp(C_6F_4)}}{\mathrm{dt}} = 3.66 \times 10^{-4} \times 21^2 = 0.1614 \text{ mm. sec}^{-1}
\]

\[
\frac{\mathrm{dp(C_4F_8)}}{\mathrm{dt}} = 19.39 \times 10^{-5} \times 142 = 0.0275 \text{ mm. sec}^{-1}
\]

Hence, the reverse reaction is occurring at more than 1/6th. of the rate of the forward reaction. A graph plotted on the basis of a second order rate equation would, therefore, be expected to deviate appreciably from a straight line after 130 seconds.

The values obtained for the velocity constant of the dimerization reaction are given in Table II.

(iii) The effect of a packed reactor.

The homogeneity of the dimerization reaction was tested by performing a series of runs at 400°, 425°, and 450°C. using a Pyrex reaction vessel packed with small pieces of Pyrex glass.

The values for the velocity constant of the dimerization reaction calculated from the results obtained agreed within the limits of experimental error with those obtained using an unpacked reaction vessel. The dimerization was, therefore, concluded to be homogeneous over the range investigated.
The velocity constant of the reaction \(2\text{C}_2\text{F}_4 = \text{C}_4\text{F}_8\) (cyclic)

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>(P_0) mm</th>
<th>(k \times 10^2) (mole/litre(^{-1}) sec(^{-1}))</th>
<th>Temp °C</th>
<th>(P_0) mm</th>
<th>(k \times 10^2) (mole/litre(^{-1}) sec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
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<td>561</td>
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</tr>
<tr>
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<td>415.5</td>
<td>115.3</td>
</tr>
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<td>219.5</td>
<td>475</td>
<td>415.5</td>
<td>393.3</td>
</tr>
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</table>

Table 11.
Table II. (continued)

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>$P_0$ mm.</th>
<th>$k \times 10^2$ (mole/litre)$^{-1}$</th>
<th>Temp °C</th>
<th>$P_0$ mm.</th>
<th>$k \times 10^2$ (mole/litre)$^{-1}$</th>
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</tbody>
</table>
(b) **The thermal decomposition of octafluorocyclobutane.**

The results obtained from the investigation of the kinetics of the dimerization reaction

\[ 2C_2F_4 = C_4F_8 \]

indicate that the reaction is reversible. The reverse reaction occurs at a sufficiently fast rate at temperatures above 450°C to effect the slope of the graph obtained from the application of the results to the second order rate equation.

The thermal decomposition of octafluorocyclobutane has been studied over the temperature range 520° to 550°C using a Pyrex reaction vessel, and over the range 550° to 590°C using a steel vessel.

Six to eight runs were carried out at each temperature and values for the velocity constant of the reaction

\[ C_4F_8 = 2C_2F_4 \]

have been calculated from the results obtained.

1. **The evaluation of \( p_0 \).**

   It was not possible to obtain a direct measure of \( p_0 \) for the reasons stated on page 138. On plotting a graph of pressure against time, using the first four or five readings obtained in each run, the points were found to lie on a smooth curve, and \( p_0 \) could be estimated reasonably accurately by extrapolation of this curve to zero time. The \( p_0 \) values derived by this method using the results obtained from the
runs performed at temperatures below 550°C were accurate to ± 0.1 mm. The accuracy decreased rapidly with temperature, however, and at 590°C, the $p_0$ values obtained could not be considered to be accurate to more than ± 0.5 mm. The values obtained for the velocity constant at 590°C were therefore only correct to ± 5% of the figures stated.

(ii) The evaluation of the velocity constant.

In evaluating the velocity constant for the decomposition of octafluorocyclobutane it was unnecessary to apply a correction for the dead space error. This error will only have a measurable effect when large pressure changes occur in the reaction vessel, as were encountered in the dimerization of tetrafluoroethylene. When octafluorocyclobutane was heated at 590°C, the total pressure change which occurred during the reaction was only 5% of the initial pressure. The dead space error will be negligible for such small pressure changes.

The velocity constant for the reaction $C_4F_8 \rightarrow 2C_2F_4$ was evaluated by three different methods:

1. Let the initial pressure inside the reaction vessel be $p_0$, and the pressure after a time $t$ be $p_t$. Then the initial concentration of octafluorocyclobutane will be proportional to $p_0$, and the concentration after a time $t$ will be proportional to $2p_0 - pt$. Substituting these terms into the integrated form of the first order rate equation, we have
A series of graphs of $t$ against $\log_{10}(2p_0 - p_t)$ were plotted. For the runs performed at 550°C and below, the points obtained from pressure readings taken during the first 90 seconds of the reaction were seen to lie on a straight line. The points obtained for longer reaction times deviated from the straight line, and the deviation increased with reaction time.

It was, therefore, concluded that the decomposition reaction behaves initially as a simple first order reaction, and values for the velocity constant were determined from the slope of the line drawn through the points obtained for short reaction times.

2. Considering the decomposition of octafluorocyclobutane as a reversible reaction, we have,

$$C_4F_8 \xrightleftharpoons[k']{k} 2C_2F_4$$

where $k$ represents the velocity constant for the decomposition of octafluorocyclobutane and $k'$ the velocity constant for the formation of octafluorocyclobutane from tetrafluoroethylene. The value for $k'$ at a particular temperature will clearly be half that given in Table II, since the latter values refer to the dimerization of tetrafluoroethylene and not the formation of octafluorocyclobutane.
Let the initial pressure in the reaction vessel be $p_0$, and the pressure after a time $t$ be $p_t$. It was observed that in the runs performed at temperatures within the range 520° to 590° C, the pressure in the reaction vessel appeared to reach a steady value after approximately 15 minutes of the reaction, and this was concluded to be the equilibrium pressure $p_e$.

The initial concentration of octafluorocyclobutane will be given by $\frac{p_0}{760RT}$ moles per litre, where $p_0$ is in millimetres and $R$ is in litre atmospheres degree$^{-1}$ mole$^{-1}$ units. The concentration of octafluorocyclobutane and tetrafluoroethylene after a time $t$ will be given by $\frac{2p_0-p_t}{760RT}$ and $\frac{2p_t-2p_0}{760RT}$ moles per litre respectively.

The nett rate of decomposition of octafluorocyclobutane is given by

$$\frac{d[x][C_4F_8]}{dt} = k\left(\frac{2p_0-p_t}{760RT}\right) - k'\left(\frac{2p_t-2p_0}{760RT}\right)^2$$

(1)

and at equilibrium,

$$k\left(\frac{2p_0-p_t}{760RT}\right) = k'\left(\frac{2p_t-2p_0}{760RT}\right)^2$$

(2)

Values for $k'$ were obtained from the figures given in Table 11, and the velocity constants for the decomposition reaction were evaluated by substituting the experimental values for $p_0$ and $p_e$ and the figures obtained for $k'$ into equation (2).

3. From equation (2) we have
\[ k' = \frac{2P_0 - P_e}{760RT} / \left( \frac{2P_0 - 2P_e}{760RT} \right)^2 \]  

(2)

Substituting the value of \( k' \) obtained from (2) into equation (1) we have

\[ \frac{d\left[C_4H_8\right]}{dt} = k\left(\frac{2P_0 - P_t}{760RT}\right) - \left(\frac{2P_0 - P_e}{760RT}\right)^2 \]  

(4)

On integration of this equation we obtain the relationship

\[ k = \frac{(P_e - P_0)}{t(3P_0 - P_e)} \times 2.303 \log_{10} \frac{P_0(P_e - P_0) + (P_t - P_0)(2P_0 - P_e)}{P_0(P_e - P_t)} \]  

(5)

It is seen from equation (5) that on plotting a graph of \( t \) against \( \log_{10} \frac{P_0(P_e - P_0) + (P_t - P_0)(2P_0 - P_e)}{P_0(P_e - P_t)} \), a straight line should be obtained of slope \( 2.303 \frac{(P_e - P_0)}{k(3P_0 - P_e)} \).

The experimental results were substituted into the above expressions, and a series of graphs were plotted. The points obtained from the results of the runs performed at temperatures over the range 550° to 590°C, using the steel reaction vessel, were found to lie on good straight lines. The results obtained from the runs performed at temperatures within the range 520° to 550°C, using the Pyrex reaction vessel, gave points which were seen to lie on a smooth curve. The curvature of these graphs increased with increase in the temperature at which the runs were performed. The velocity constants were calculated from the initial slopes of these graphs.

The values for the velocity constant of the decomposition
FIGURE 35
Pyrolysis of octafluorocyclobutane
at 550°C in Pyrex vessel.

FIGURE 36
Pyrolysis of octafluorocyclobutane
at 520°C in Pyrex vessel.
reaction calculated from the results obtained in each run by the three methods described above, are given in Table 12.

Considering first the values obtained for the velocity constant from the results of runs performed using the Pyrex vessel. The values obtained by Method 3 are, in general, similar to, but slightly lower than those obtained by Method 1. The fact that the graphs obtained by Method 3 are not straight lines, however, indicates that the pressure changes occurring in the reaction vessel are not in accord with that for a first order reaction moving to equilibrium with a second order reaction. The results obtained for any one temperature by Method 2, whilst agreeing reasonably well with each other, are appreciably greater than those obtained by Methods 1 and 3, for the same temperature.

The reason for this disagreement between the results obtained by the three methods became apparent when a sample of octafluorocyclobutane was heated over a long period of time at 550°C. in the Pyrex vessel. It was found that the pressure inside the vessel did not, in fact, settle to a steady equilibrium value, but continued to rise very slowly and steadily for an indefinite period. The graph obtained on plotting pressure change against reaction time for the run carried out at 550°C, is shown in Figure 35. An examination of the products obtained from this run indicated the presence of a small amount
of carbon monoxide, and it was therefore concluded that either
the tetrafluoroethylene formed or the octafluorocyclobutane
were reacting with the walls of the reaction vessel according
to the equation

$$\text{C}_2\text{F}_4 + \text{SiO}_2 = \text{SiF}_4 + 2\text{CO}. \quad (6)$$

The mean of the values obtained by Method 1 for the
velocity constant of the decomposition reaction at 520°C was
used to evaluate $p_e$ and a series of values for $p_t$ by substitution
into equations (2) and (4). A theoretical curve of pressure
against time was then plotted from the figures obtained, and
this was compared with the graph of the experimental values
obtained in a run performed at 520°C. The theoretical and
experimental curves are shown in Figure 36. Assuming that the
value taken for the velocity constant of the decomposition
reaction is correct, then it appears that at 520°C a reaction
such as (6) occurs, giving rise to a larger increase in
pressure than will occur with the reaction

$$2\text{C}_2\text{F}_4 \rightleftharpoons \text{C}_4\text{F}_8$$

It was therefore concluded that over the temperature range
520° to 550°C a reaction was occurring between the gases in the
Pyrex vessel and the walls of the vessel. Hence the figures
taken for $p_e$ must be incorrect, and therefore, the values
obtained for $k$ by Methods 2 and 3 must also be incorrect.

The Pyrex vessel was replaced by a steel vessel, and
a series of runs were performed at 550°, 570°, and 590° C. During preliminary runs it was found that the reaction products again contained small amounts of carbon monoxide. This was concluded to be formed by a reaction between the gases in the steel vessel and small amounts of iron oxide on the inner walls of the vessel. Precautions were, therefore, taken to remove any oxide scale from the inside of the vessel before use.

It was found that using the clean vessel, the pressure of the reacting gases settled to a steady equilibrium value, and on prolonged heating, no subsequent rise in pressure occurred. Values for the velocity constant of the decomposition reaction were calculated from the results obtained, using Methods 1, 2, and 3. Straight line graphs were obtained by Method 3. This indicated that in the steel vessel the pressure changes occurring were those to be expected for a first order reaction moving to equilibrium with a second order reaction. It is seen from Table 12, that the three sets of values obtained for the velocity constant at 550° C. are in good agreement with each other, and further, that they agree with those obtained by Method 1 from the results of the runs performed at 550° C. using the Pyrex vessel. It may reasonably be concluded, therefore, that these latter values are not affected by reaction (6) since this reaction does not occur in the steel vessel. Hence, the values obtained by Method 1 for
the velocity constant of the decomposition reaction over the range $520^\circ \text{C}$ to $550^\circ \text{C}$, from the results of the runs performed using the Pyrex vessel, may be assumed to be correct within the limits of experimental error.

It is seen from Figure 36, that at $520^\circ \text{C}$, the effect of reaction (6) on the pressure of the reacting gases does not become apparent until after approximately 3 minutes reaction time. Since the velocity constant was calculated using only the pressure figures obtained during the first 90 seconds of the reaction, no error due to reaction (6) will arise.
Table 12.
The velocity constant of the decomposition reaction
\[ C_4H_8(\text{cyclic}) = 2C_2H_4 \quad (k \times 10^5 \text{sec}^{-1}) \]

<table>
<thead>
<tr>
<th>Temp (^{\circC})</th>
<th>( P_0 ) mm.</th>
<th>Method 1.</th>
<th>Method 2.</th>
<th>Method 3.</th>
</tr>
</thead>
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<tr>
<td>351.0</td>
<td>3.52</td>
<td>5.18</td>
<td>3.42</td>
<td></td>
</tr>
<tr>
<td>437.5</td>
<td>3.50</td>
<td>5.52</td>
<td>3.76</td>
<td></td>
</tr>
<tr>
<td>520 P</td>
<td>444.9</td>
<td>3.52</td>
<td>5.32</td>
<td>3.41</td>
</tr>
<tr>
<td>415.1</td>
<td>3.55</td>
<td>5.80</td>
<td>3.50</td>
<td></td>
</tr>
<tr>
<td>381.1</td>
<td>4.01</td>
<td>5.90</td>
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<tr>
<td>348.0</td>
<td>6.44</td>
<td>11.20</td>
<td>6.13</td>
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<tr>
<td>377.9</td>
<td>6.71</td>
<td>10.44</td>
<td>5.80</td>
<td></td>
</tr>
<tr>
<td>530 P</td>
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<td>10.34</td>
<td>5.62</td>
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<td>5.32</td>
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<td>361.8</td>
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<td>9.62</td>
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<td>411.2</td>
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<td>9.55</td>
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<tr>
<td>540 P</td>
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<td>12.76</td>
<td>18.78</td>
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<td>356.3</td>
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<td>406.4</td>
<td>19.52</td>
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</table>

\( P = \text{Pyrex reaction vessel.} \)
<table>
<thead>
<tr>
<th></th>
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</thead>
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<td>56.46</td>
</tr>
<tr>
<td>590 St</td>
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<tr>
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<td>175.0</td>
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\( St = \) steel reaction vessel.
**Figure 37.**

Graph of $\log_{10} k$ against $\frac{1}{T}$

For reaction $2C_2F_4 \rightarrow C_4F_8$ (cyclic)
Figure 38

Graph of $\log_{10} k$ against $\frac{1}{T}$

For reaction $\text{C}_2\text{F}_6(\text{cyclic}) \rightarrow 2\text{C}_2\text{F}_4$. 

$\log_{10} k$ values are plotted against $\frac{1}{T} \times 10^4$. 

The graph shows a straight line, indicating an Arrhenius relationship.
(c) The application of the reaction rate theories to the experimental results.

(i) The evaluation of the activation energies.

A graph of \( \log_{10}k \) against \( 1/T \) was plotted using the values given in Table 11 for the velocity constant of the dimerization reaction. The points were seen to lie on a straight line (Figure 37), and from the slope of the line, a figure of 25.4 k.cal. was obtained for the energy of activation of the reaction

\[ 2C_2F_4 = C_4F_8(\text{cyclic}) \quad (1) \]

The figures obtained by Method 1 for the velocity constant of the decomposition reaction (Table 12), were used to plot a graph of \( \log_{10}k \) against \( 1/T \). The mean of the experimental figures obtained for \( k \) at each temperature was used to evaluate \( \log_{10}k \). A straight line graph was obtained (Figure 38), and from the slope of the line the energy of activation of the reaction

\[ C_4F_8(\text{cyclic}) = 2C_2F_4 \quad (2) \]

was found to be 74.1 k.cal.

From the values obtained for the energies of activation of reactions (1) and (2), the heat of reaction at constant volume (\( \Delta E \)) is found to be -48.7 k.cal. On substituting this figure into the equation

\[ \Delta E = \Delta H - RT\Delta n \quad (2) \]
where \( \Delta H \) represents the heat of reaction at constant pressure and \( \Delta n \) is the increase in the number of gas molecules in the reaction, a value of -50.3 k.cal. is obtained for \( \Delta H \) at 800° absolute.

(ii) **The probability factor of the dimerization reaction.**

According to the kinetic theory of gases, the number of molecules colliding per second in one millilitre of gas when the concentration of reactants is \( n \) molecules per millilitre is given by

\[
z = 4n^2 \sigma^2 \left( \frac{\pi RT}{M} \right)^{\frac{1}{2}}
\]  

(4)

where \( \sigma \) is the molecular collision diameter, and \( M \) the molecular weight of the gas. If the energy of activation for reaction between the molecules is \( E \), that is the minimum energy which the colliding molecules must possess before they can react. Then according to the simple collision theory, the number of molecules reacting is \( z e^{-E/RT} \) per ml. per sec. Hence

\[
k = \frac{z e^{-E/RT}}{6.023 \times 10^{20}} \text{ litre-mole}^{-1} \text{ sec}^{-1}
\]  

(5)

From equations (4) and (5) we have

\[
k = \frac{4n^2 \sigma^2}{6.023 \times 10^{20}} \left( \frac{\pi RT}{M} \right)^{\frac{1}{2}} e^{-E/RT} \text{ litre-mole}^{-1} \text{ sec}^{-1}
\]  

(6)

The energy of activation of the reaction \( 2C_2F_4 = C_4F_8 \) (cyclic) has been found to be 25.4 k.cal. The molecular diameter of tetrafluoroethylene was calculated using the equation
\[ \sigma = 1.33 \times 10^{-8} \frac{3}{v} \]  

(1)

where \( \sigma \) is the molar diameter, and \( v \) is the molar volume (i.e., molecular weight/density of the liquid at the boiling point)(98). For a concentration of 1 mole per litre, \( n \) in equation (6) is \( 6.023 \times 10^{20} \).

On substituting the values for \( E \), \( n \), and \( \sigma \) into equation (6) a figure of 1614 litre-mole\(^{-1}\)sec\(^{-1}\) was obtained for the velocity constant of the dimerization reaction at 400°C. Now the experimental value for \( k \) at this temperature is 0.613 litre-mole\(^{-1}\)sec\(^{-1}\), and hence, the probability factor \( P \) in the equation

\[ k = P e^{-E/RT} \]  

(8)

is \( 5.65 \times 10^{-4} \).

(iii) The frequency factor for the decomposition reaction.

By substituting the experimental values for the velocity constant at 520°C and the energy of activation of the reaction \( C_4F_8 = 2C_2F_4 \) into the equation

\[ k = Ae^{-E/RT} \]  

(10)

\( A \) was found to be \( 8.9 \times 10^{15} \) sec\(^{-1}\).

(iv) The heat and entropy of dimerization of tetrafluoroethylene.

According to the van't Hoff isotherm,

\[ \Delta G^o_p = -RT \log e K_p \]  

(11)

where \( \Delta G^o_p \) is the standard free energy change, and \( K_p \) the equilibrium constant of the reaction, the standard state
of each reactant being unit pressure.

Now

\[ \Delta G_p^o = \Delta H^o - T \Delta S_p^o \]  

(12)

Assuming the system behaves ideally, \( \Delta H^o \), the standard change in heat content, may be replaced by \( \Delta H \) without specifying the standard states. Hence from equations (11) and (12) we have

\[ \log e K_p = \frac{\Delta S_p^o}{R} - \frac{\Delta H}{RT} \]  

(13)

The experimental results given above are expressed in concentration units, hence it will be more convenient to consider \( K_c \), where the standard state is unit concentration rather than \( K_p \). The transformation may be made by means of the expression

\[ \log e K_p = \log e K_c + \Delta n \log e RT \]  

(14)

In the reaction \( 2C_2F_4 \rightarrow C_4F_8 \) the increase in the number of molecules, \( \Delta n \), is -1. Hence equation (14) becomes

\[ \log e K_p = \log e K_c \]  

(15)

Thus equation (13) may be expressed in the more convenient form

\[ \log_{10} \frac{K_c}{T} = \frac{\Delta S_p^o}{2.303R} - \frac{\Delta H}{2.303RT} + \log_{10} R \]  

(16)

The value of \( K_c \) at 800° abs. was calculated from the experimental figures for the velocity constant of the dimerization reaction, and of the decomposition reaction. \( \Delta H \), the heat of reaction at constant pressure has been found to have a value of -50.3 k.cal. at 800° abs. (see page 163). On substituting this figure, and the value obtained for \( K_c \) at
800\textdegree\, abs. into equation (16) \( \Delta S^0 \) at 800\textdegree\, abs. was found to be
-49.2 cal. per degree.

(v) The application of the theory of absolute reaction rates to the experimental results.

According to the theory of absolute reaction rates (19), before two, or more molecules possessing the requisite energy can react, they must first collide and form the activated complex for the reaction, which then either decomposes to the products of reaction, or reforms the initial reactants. Thus

\[ A + B + \ldots = \text{Product} \]

The initial reactants are, therefore, always in equilibrium with the activated complexes, and the latter decompose to products at a definite rate. It is assumed that the reaction does not appreciably disturb the equilibrium concentration of activated complexes.

In the statistical calculation of reaction rates the activated complex is treated just like a normal molecule, except that in addition to having three translational degrees of freedom, it has a fourth degree of freedom along the reaction coordinate. To compensate for this, the activated complex is assumed to have one stiff vibration so that the particular frequency is extremely large. It can then be shown that

\[
k = \kappa \frac{k_b T}{h} \text{K}^+ \quad (17)
\]

where \( k \) is the velocity constant of a reaction, \( \kappa \) is the
transmission coefficient, which allows for the possibility that not every activated complex reaching the top of the energy barrier and moving along the coordinate of decomposition, leads to reaction. \( k \) and \( h \) are the Boltzmann and Planck constants respectively, and \( K^* \) is the constant for the equilibrium between the reactants and the activated complex.

The equilibrium constant \( K^* \) may be expressed in terms of the standard free energy of the process by means of the thermodynamic equation

\[
-\Delta G^* = RT \log_e K^* \tag{18}
\]

where \( \Delta G^* \) is the standard free energy of the activation process. We then have from equations (17) and (18)

\[
k = \frac{k_B T}{h} e^{-\Delta G^* / RT} \tag{19}
\]

The transmission coefficient is omitted from equation (19) since it will later be assumed to be unity.

Since \( \Delta G^* = \Delta H^* - T \Delta S^* \), we have from equation (19)

\[
k = \frac{k_B T}{h} e^{-\Delta H^* / RT} e^{-\Delta S^* / R} \tag{20}
\]

where \( \Delta H^* \) and \( \Delta S^* \) are the standard heat and entropy changes, respectively, accompanying the activation process.

In order to evaluate \( \Delta S^* \) from the experimental results, equation (20) must be rearranged to a form containing the experimental activation energy in place of \( \Delta H^* \).

Equation (17) may be written in the logarithmic form
\[ \log_e k_c = \log_e k_n^s + \log_e T + \log_e K_c^e \]  
(21)

where \( k_c \) and \( K_c^e \) refer to the rate and equilibrium constants, respectively, in terms of concentration units.

Differentiating equation (21) with respect to temperature we have

\[ \frac{d \log_e k_c}{dT} = \frac{1}{T} + \frac{d \log_e K_c^e}{dT} \]  
(22)

Now \( \frac{d \log_e k_c}{dT} = \frac{E}{RT^2} \), where \( E \) is the experimental energy of activation. Hence equation (22) becomes

\[ \frac{E}{RT^2} = \frac{1}{T} + \frac{d \log_e K_c^e}{dT} \]  
(23)

The last term in equation (23) is equal to \( \frac{\Delta E^*}{RT} \) where \( \Delta E^* \) is the increase in the internal energy for the activation process, or the heat of activation at constant volume. Hence

\[ E = RT + \Delta E^* \]  
(24)

Now \( \Delta E^* = \Delta H^* - \Delta n^*RT \), where \( \Delta n^* \) is the increase in the number of molecules when the activated state is formed from the reactants, and therefore, equation (24) may be written

\[ \Delta H^* = E - RT(1-\Delta n) \]  
(25)

Substituting this expression for \( \Delta H^* \) into equation (20) we have

\[ k_c = e^{-(\Delta n^*-1) \frac{k_n T}{n} e^{-E/RT}} e^{-\Delta S^e_c/R} \]  
(26)

It can be shown thermodynamically that for an ideal gas

\[ \Delta S_c = \Delta S_p - \Delta n R \log_e RT \]
Thus \( e^{\frac{\Delta S_p^*/R}{T}} = e^{\frac{\Delta S_p^*/R}{(RT)^{-\Delta n^*}}} \)

so that equation (26) becomes

\[ k_c = e^{-(\Delta n^* - 1) \frac{k_B T}{h}} e^{-E/RT} e^{\Delta S_p^*/R (RT)^{-\Delta n^*}} \quad (27) \]

For the reaction \( 2C_2F_4 \rightarrow C_4F_8 \), \( \Delta n^* = -1 \), hence equation (27) becomes

\[ k_c = e^{2 \frac{k_B T}{h}} e^{-E/RT} e^{\Delta S_p^*/R (RT)} \quad (28) \]

The velocity constant for the reaction \( 2C_2F_4 \rightarrow C_4F_8 \)
at 800°C abs. is 12.04 l.-mole\(^{-1}\)sec\(^{-1}\) This constant, by definition, refers to the rate of disappearance of tetrafluoroethylene, whereas \( k_c \) in equation (28) is the rate constant for the formation of the product. Hence, \( k_c = \frac{12.04}{2} \). Substituting this value into equation (28) together with the experimental value for the energy of activation, we obtain a figure of -38.4 cal.pere degree for \( \Delta s_p^* \) at 800°C abs.

\( \Delta h_p^* \) was found to be 22.2 k.cal. at 800°C abs. by substitution of the experimental activation energy into equation (25).

For the decomposition reaction \( C_4F_8 \text{(cyclic)} \rightarrow 2C_2F_4 \), \( \Delta n^* = 0 \), and hence equation (27) becomes

\[ k_c = e^{\frac{k_B T}{h}} e^{-E/RT} e^{\Delta S_p^*/R} \quad (29) \]

Substituting the experimental value for the velocity constant at 527°C, and the energy of activation of the decomposition reaction into equation (29), \( \Delta s_p^* \) at 800°C abs. is found to be 10.57 cal. per degree, this value being independent of the
Figure 39

Graph of $\log_{10} K_c$ against $\frac{1}{T}$

For reaction $2C_2F_4 \rightleftharpoons C_4F_8$ (cyclic)
standard state chosen.

From equation (25) \( \Delta H^\circ \) for the decomposition reaction was found to be 72.6 k.cal. at 800° abs.

A value of -48.1 k.cal. was obtained for \( \Delta E \) from the slope of the graph of \( \log_{10} K_c \) against \( 1/T \) (Figure 39). Values for \( K_c \), the equilibrium constant of the reaction \( 2C_2F_4 \rightleftharpoons C_4F_8(cyclic) \), were calculated from the experimental values for the velocity constants of the forward and reverse reactions obtained at temperatures between 520° and 590°C.

**Table 13.**

**Classical Theory Constants.**

\[
2C_2F_4 = C_4F_8(cyclic) \quad C_4F_8(cyclic) = 2C_2F_4
\]

\[
( k = F_\alpha e^{-E/RT} ) \quad ( k = A e^{-E/RT} )
\]

\[
E = 25.4 \text{ k.cal.} \quad E = 74.1 \text{ k.cal.}
\]

\[
P = 3.85 \times 10^{-4} \quad A = 8.9 \times 10^{15} \text{ sec}^{-1}
\]

\[ \Delta E \rightleftharpoons \text{by difference} = -48.7 \text{ k.cal.} \]

\[ \Delta E \rightleftharpoons \text{from the equilibrium constant} = -48.1 \text{ k.cal.} \]

\[ \Delta H = -50.3 \text{ k.cal. at 800° abs.} \]

\[ \Delta S^\circ = -49.2 \text{ cal/° per degree at 800° abs.} \]

**Absolute Reaction Rate Theory Constants.**

\[
2C_2F_4 = C_4F_8(cyclic) \quad C_4F_8(cyclic) = 2C_2F_4
\]

\[ \Delta S^\circ \rightleftharpoons \text{at 800° abs.} = -38.4 \text{ cal/°} \]

\[ \Delta H^\circ \rightleftharpoons \text{at 800° abs.} = 72.6 \text{ k.cal.} \]
PART IV: DISCUSSION.

The discussion has for convenience been considered in two parts. The results obtained from the work described in Part II of the thesis are considered in Section (a) of the discussion. Section (b) contains a discussion of the kinetics of the dimerization of tetrafluoroethylene and of the decomposition of octafluorocyclobutane. This second section is based on the results obtained from the work described in Part III of the thesis.

(a) The thermal reactions of tetrafluoroethylene.

The results obtained from the study of the pyrolysis of tetrafluoroethylene over the temperature range 300° to 800° C. using the flow system, show an increasing complexity of reaction as the temperature rises. This makes it convenient for discussion to divide the temperature range into three regions, 300° to 500° C., 600° to 700° C., and 800° C.

(1) 300° to 500° C.

At 300° to 500° C. the major reaction occurring is the dimerization of tetrafluoroethylene to give octafluorocyclobutane,

\[ 2C_2F_4 = C_4F_8(\text{cyclic}) \]  (1)

It has been found, from the investigation of the kinetics of the dimerization reaction, that reaction (1) is reversible, although at 500° C. the reverse reaction

\[ C_4F_8(\text{cyclic}) = 2C_2F_4 \]  (2)
is very slow. Thus at 1 atmosphere pressure and 500°C, the position of equilibrium corresponds to less than 2% by volume of tetrafluoroethylene.

In accordance with the recently reported results of the investigation of the thermal decomposition of tetrafluoroethylene (5) (see Table 14), it is seen from Table 4, that no butenes are formed at 500°C. or below. Both dimerization to a butene and reorganization of the octafluorocyclobutane to a butene require a transfer of a fluorine atom from carbon to carbon, a transfer which must have a high activation energy compared with a similar transfer of a hydrogen atom.

(ii) 600°C to 700°C.

At 600°C and 700°C, the occurrence of fluorine atom transfers is shown by the formation of butenes and hexafluoropropene. Since the products of pyrolysis at 700°C contain appreciable quantities of butene, it seems reasonable to conclude that the small volume of undistilled liquid boiling above -5.5°C, which remained in the distilling column after distillation of the products of pyrolysis at 600°C, also contained some butenes. The liquid resembled C₄ fluorocarbons in that it was highly volatile at temperatures between -5°C and +15°C.

The butenes found among the products of pyrolysis may be formed both by reorganization of octafluorocyclobutane
and in one step by dimerization of tetrafluoroethylene, i.e.

$$2C_2F_4 \rightarrow C_4F_8(\text{cyclic}) = C_4F_8(\text{butene}) \quad (3)$$

From the values obtained for the velocity constants of the dimerization and decomposition reactions, it was found that at 600°C and 1 atmosphere pressure, the position of equilibrium of the reaction

$$2C_2F_4 \Rightarrow C_4F_8(\text{cyclic}) \quad (5)$$
corresponds to approximately 5% by volume of tetrafluoroethylene. Hence the volumes of tetrafluoroethylene and octafluorocyclobutane found in the products of pyrolysis at 600°C, indicate that these two gases were close to their equilibrium concentrations. At 700°C, the equilibrium mixture should contain roughly 8% by volume of tetrafluoroethylene. The second part of reaction (3) will disturb the equilibrium (5) by causing a decrease in the partial pressure of octafluorocyclobutane. The equilibrium will be restored by dimerization of the small percentage of tetrafluoroethylene present. Similarly reaction (4) will cause a decrease in the amount of tetrafluoroethylene present and the equilibrium (5) will be restored by dissociation of the octafluorocyclobutane. Thus either reaction (3) or reaction (4) will cause a decrease in the amount of both the tetrafluoroethylene and the octafluorocyclobutane present in the reacting gases. This accounts for the fact that
whereas the products of pyrolysis of tetrafluoroethylene at 700°C. contain large volumes of octafluorobutenes, neither tetrafluoroethylene, nor octafluorocyclobutane was present.

It appears from the results given in Table 4, that hexafluoropropene occurs in the products of pyrolysis of tetrafluoroethylene only when perfluorobutenes are also present. It is possible, therefore that hexafluoropropene is formed by the reaction

\[
C_4F_8(\text{butene}) + C_2F_4 = 2C_3F_6 \tag{6}
\]

Only octafluorobutene-2, which is formed in good yield at 700°C., can undergo reaction (6) without reorganization of carbon-fluorine bonds, and the largest yield of hexafluoropropene is obtained at 700°C.

In the recently reported investigation of the thermal reactions of tetrafluoroethylene and octafluorocyclobutane (5), it was found that hexafluoropropene was formed at temperatures below that necessary for the formation of butenes. The results obtained in this investigation are given in Table 14. It is noted that the products of pyrolysis of tetrafluoroethylene at 700°C. are the same as those obtained by the pyrolysis of octafluorocyclobutane at 700°C. (see Tables 4 and 14), and the products are obtained in similar yields. This is as would be expected from the mechanisms proposed above.

It is seen from Table 14 that the products of pyrolysis
of tetrafluoroethylene at 550°C contain an appreciable quantity of hexafluoropropene, whereas octafluorobutenes are absent. This difference in behaviour may be due to the fact that in the previous investigation, a reaction vessel packed with graphite was used in the flow apparatus. These conditions would favour any heterogeneous reactions occurring in the system, and it is possible that the hexafluoropropene formed at 550°C was produced by a reaction of this type. The experimental conditions employed in the investigation reported here did not favour heterogeneous reactions, and this may account for the fact that hexafluoropropene was obtained in a comparatively low yield at 600°C.

Table 14.
The pyrolysis of tetrafluoroethylene and octafluorocyclobutane. (Miller) (Ref. 5)

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Fraction 1. CF₂=CF₂</th>
<th>Fraction 2. C₄F₈ (cyclic)</th>
<th>Fraction 3. CF₃-CF₂-CF=CF₂</th>
<th>Residue. wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>435±5°</td>
<td>0</td>
<td>28</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>550±10°</td>
<td>12</td>
<td>71</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>640±10°</td>
<td>26</td>
<td>52</td>
<td>14</td>
<td>6</td>
</tr>
<tr>
<td>655±5°</td>
<td>42</td>
<td>16</td>
<td>19</td>
<td>6</td>
</tr>
<tr>
<td>750±10°</td>
<td>4</td>
<td>0</td>
<td>44</td>
<td>11</td>
</tr>
<tr>
<td>700±5°</td>
<td>37</td>
<td>0</td>
<td>48</td>
<td>11</td>
</tr>
</tbody>
</table>
In order to account for the large yields of hexafluoropropene which were obtained at temperatures below that necessary for the formation of octafluorobutene, it was suggested (5) that hexafluoropropene was formed by addition of a difluoromethylene radical to tetrafluoroethylene followed by rearrangement, i.e.

\[ \text{CF}_2 \cdot + \text{C}_2\text{F}_4 = \text{C}_3\text{F}_6 \cdot \]  

(7)

\[ \text{C}_3\text{F}_6 \cdot = \text{C}_3\text{F}_6 \text{(propene)} \]  

(8)

Difluoromethylene radicals may also be formed by the reaction

\[ \text{C}_2\text{F}_4 = \text{CF}_2 \cdot + \text{CF}_2 \cdot \]  

(2)

or by the reaction

\[ 2\text{C}_2\text{F}_4 = \text{C}_3\text{F}_6 \cdot + \text{CF}_2 \cdot \]  

(10)

The latter mechanism was suggested by Lewis and Naylor (74) to account for the formation of hexafluoropropene by the thermal decomposition of tetrafluoroethylene polymer.

Although reactions of the type (7)(8)(2) and (10) may take place in a packed reaction vessel at 550°C, and above, the results given in Table 4 do not indicate the occurrence of free radical reactions. In the investigation of the mercury photosensitized reactions of tetrafluoroethylene (1), it was found that reaction (7) is followed by either a chain polymerization reaction leading to the formation of a high polymer of tetrafluoroethylene, or to cyclization of the \( \text{C}_3\text{F}_6 \cdot \) diradical to hexafluorocyclopropane. Hence we should expect
that if the hexafluoropropene obtained at 600° and 700°C. was formed by reactions (7) and (8), then appreciable quantities of the high polymer of tetrafluoroethylene would be formed at the same time. Only a minute trace of solid (or liquid) high polymer of tetrafluoroethylene was obtained from the pyrolysis of tetrafluoroethylene at these temperatures, however. It is, therefore, most probable that the hexafluoropropene obtained at 600° and 700°C. was formed by a reaction such as (6) rather than by (7) and (8).

It has been shown (page 13) that the energy of activation for the dissociation of ethylene into two methylene radicals is unlikely to be less than 120 k.cal. Reaction (9) is basically the same as the corresponding reaction of ethylene, but the energy of activation of the reaction is expected to be less, since it has been pointed out (1), that by analogy with the electronic structure of carbon dioxide (100), the difluoromethylene radical in the singlet state will be stabilized by overlap of the \( ^p \) orbitals of the carbon and fluorine atoms. Insufficient data are available to calculate an accurate value for the energy of activation of (9), but a rather high value for the resonance energy of the difluoromethylene radical would be required to permit the dissociation of tetrafluoroethylene at 600° and 700°C.

The dimerization reaction leading to the formation of
a difluoromethyl and a $\text{C}_3\text{F}_6^\cdot$ radical (reaction 10) cannot be ruled out on energy grounds, but as has already been mentioned, the absence of the high polymer of tetrafluoroethylene in the products of pyrolysis at 600° and 700°C, suggests that this reaction does not occur.

It is seen from Table 4, that in the runs performed at 400° and 600°C, using the steel reaction vessel, the yields of the various products obtained are almost equal to the corresponding yields obtained using the silica vessel. The rates of flow of tetrafluoroethylene through the two vessels were adjusted to give approximately equal reaction times, and hence it can be concluded that the steel vessel had no measurable catalytic effect on any of the reactions occurring during pyrolysis.

The occurrence of carbon monoxide and silicon tetrafluoride in the products of pyrolysis of tetrafluoroethylene at 700°C, using the silica reaction vessel, indicates that the gas was reacting with the silica of the reaction vessel according to the equation

$$\text{C}_2\text{F}_4 + \text{SiO}_2 = \text{SiF}_4 + 2\text{CO}$$

(iii) 800°C.

At all temperatures below 800°C, the products of pyrolysis of tetrafluoroethylene have the general formula $(\text{CF}_2)_n$. At 800°C, a quite different type of reaction occurs
yielding saturated products of low molecular weight and highly unsaturated products of high molecular weight. Earlier investigators report the formation of low molecular weight saturated products and high boiling residues at temperatures above 600°C. (5) but give little indication as to the nature or yield of these compounds. The lower temperature of formation of these compounds in the previous investigation may again be due to the effect of the packing in the reaction vessel.

From the nature and yield of the products of pyrolysis of tetrafluoroethylene at temperatures below 800°C, it is apparent that the rate of formation of the octafluorobutenes at 800°C, will be very fast. It is probable, therefore, that the saturated and highly unsaturated products obtained at this temperature may arise from the decomposition of the octafluorobutenes. At 800°C, only octafluorobutene-1 was detected in the products of pyrolysis.

The energy of activation for the reaction

$$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 \rightarrow \text{CH}_3^- + \text{CH}_2=\text{CH}=\text{CH}_2 \quad (12)$$

has been shown to be 62 ± 2 k.cal. (22). The energy of activation for the reaction

$$\text{CF}_3\text{CF}_2\text{CF}=\text{CF}_2 \rightarrow \text{CF}_3^- + \text{CF}_2=\text{CF}=\text{CF}_2 \quad (13)$$

must be similar since only the rupture of a C-C bond is involved, and hence at 800°C, reaction (13) must be a fast reaction. The products formed at 800°C are in accord with the
occurrence of (13) as a major reaction at this temperature.

Whilst hexafluoroethane is obtained in large yield at 800°C, only a trace of carbon tetrafluoride is formed. This suggests that the trifluoromethyl radicals formed by reaction (13) will tend to unite, ie.

\[
\text{CF}_3^- + \text{CF}_3^- \rightarrow \text{C}_2\text{F}_6
\]  \hspace{1cm} (14)

rather than react by abstraction of fluorine from a molecule, ie.

\[
\text{CF}_3^- + \text{RF} \rightarrow \text{CF}_4 + \text{R}^-
\]  \hspace{1cm} (15)

Polymerization initiated by the free radicals, ie.

\[
\text{R}^- + \text{C}_4\text{F}_8 = \text{R}_1^- \text{ etc.}
\]  \hspace{1cm} (16)

accounts for the formation of high molecular weight products, but the high yield of hexafluoroethane and the correspondingly high unsaturation of the liquid products requires that there must be a further complex series of degradation and polymerization reactions. The following types of reactions can be expected to occur,

\[
2\text{CF}_5 = \text{C}_6\text{F}_{10}
\]

\[
\text{C}_6\text{F}_{10} = \text{CF}_3^- + \text{R}^-
\]

\[
\text{R}^- + \text{R'}^- \rightarrow \text{R}^1\text{R}^2
\]

\[
\text{R}^1\text{R}^2 = \text{CF}_3^- + \text{R}^{n'}^-\text{ etc.}
\]

(b) The kinetics of the dimerization of tetrafluoroethylene and the decomposition of octafluorocyclobutane.

Before passing to a discussion of the results obtained from the investigation of the kinetics of the
reaction $2C_2H_4 \rightleftharpoons C_4H_8$ (cyclic) it will be convenient to consider first the kinetics of the dimerization reactions of ethylene and of the reverse reactions.

(1) The dimerization of ethylene.

At temperatures in the region of 300° to 500°C. and at high pressures, ethylene dimerizes to give butylene. Pease obtained a value of 35 k. cal. for the energy of activation of the reaction

$$2C_2H_4 = C_4H_8 \text{(butene)}$$

On substituting this figure into the equation

$$k = Pz e^{-E/RT}$$

$P$ is found to be approximately $5 \times 10^{-4}$. Thus the observed rate of polymerization of ethylene is about 2000 times slower than they calculated by the simple collision theory.

If the specific reaction rate, $k$, is expressed in terms of concentrations, then according to the theory of absolute reaction rates it can be represented, for a bimolecular gas reaction, by either of the expressions

$$k = e^2 \frac{k_BT}{h} e^{\Delta S^e/R_e - E/RT}$$

or

$$k = e^2 \frac{k_BT}{RT} e^{\Delta S^p/R_e - E/RT}$$

where $\Delta S^e$ and $\Delta S^p$ are the entropies of activation with unit concentration or unit pressure, respectively, as the standard state, and $E$ is the experimental energy of activation (99). Combining equations (2) and (3) we have
If the specific reaction rate is expressed in cc. mole\(^{-1}\) sec\(^{-1}\) units, so that the standard state is a concentration of 1 mole per cc., then \(z\) is of the order of \(10^{14}\) for binary collisions. The term \(e^2 \frac{k_BT}{h}\) is approximately \(5 \times 10^{13}\) at ordinary temperatures. Thus if the simple collision theory holds for a reaction, i.e., if \(P\) is unity, then \(e^{\frac{\Delta S^e}{R}}\) for the standard state mentioned, will have a value of approximately 2. Hence, when the simple collision theory is applicable to a reaction, the entropy of activation, the standard state being a concentration of 1 mole per cc. of gas, should be of the order of 1 calorie per degree per mole.

When a reaction occurs between two simple molecules, the formation of the activated state requires little rearrangement of energy between the various degrees of freedom. Thus \(\Delta S^e\) will have a small positive or negative value. The simple collision theory should be applicable to reactions of this type, since nearly every collision between molecules possessing the requisite energy should lead to a chemical reaction. When a reaction occurs between complex molecules, however, there will be a considerable rearrangement of energy among the degrees of freedom. There will, therefore, be a decrease in entropy on the formation of the activated complex, i.e., \(\Delta S^e\) will have a large negative value. In these reactions only a
small fraction of the collisions between activated molecules will be expected to lead to a chemical reaction, and hence $P$ should be less than unity.

The dimerization of ethylene appears to be a reaction of this latter type. The value obtained for the probability factor indicates that only one collision in 2000 between activated molecules results in a reaction.

The difference of entropy between a mole of butene-1 and two moles of ethylene has been calculated by Fitler (101) to be -30.1 cal./degree, the standard states being the ideal gases at 1 atmosphere pressure and 25°C, in each case. Jahn (107) assumed that the activated complex formed in reaction (1) (page 181) has a structure similar to that of butene-1. The activated complex can be treated as a normal molecule with one very stiff vibrational mode, and since the entropy contribution of this lost vibrational mode will be small, the difference in entropy between one mole of butene-1 and the activated complex will also be small. Thus, Jahn assumed that for the dimerization reaction, $\Delta S_p^\circ$, under the conditions mentioned, is roughly -30.1 cal./degree.

In order to make a direct comparison with the values obtained for the entropy of activation of the dimerization reaction of tetrafluoroethylene, we require to know $\Delta S_p^\circ$ at 800°C abs. This can be calculated from the equation
\[ \Delta S_p^\circ = -30.1 - 3R \log_e \frac{T}{298} \]  \hspace{1cm} (6)

This equation is derived from the standard equation for the change of entropy with temperature, assuming that the difference in heat capacities lies in the three translational and three rotational degrees of freedom which disappear when two molecules of ethylene are converted into the activated complex (102).

From equation (6), \( \Delta S_p^\circ \) for the dimerization of ethylene at 800° abs. is found to be -36.0 cal./degree. In order to obtain \( \Delta S_c^\circ \), the above figure for \( \Delta S_p^\circ \) is substituted into the equation (99)

\[ \Delta S_c^\circ = \Delta S_p^\circ + R \log_e pv \]  \hspace{1cm} (7)

In the present case \( p \) is 1 atmosphere, and \( v \) is the volume in cubic centimetres occupied by one mole of gas at 800° abs. By this method, \( \Delta S_c^\circ \) at 800° abs. is found to be -13.5 cal./degree.

This large negative value for the entropy of activation of the dimerization of ethylene and the correspondingly low value for the probability factor are in accord with the theory outlined above, and indicate that the formation of the activated complex from two molecules of ethylene requires energy changes in several degrees of freedom. There is, therefore, a low probability of chemical reaction when a collision occurs between activated molecules.

Substituting the value for the experimental activation
energy into the equation

\[ E = RT + \Delta H^\circ - \Delta n^\circ RT \]  

(8)
a value of 31.8 k.cal. is obtained for the heat of activation of the dimerization reaction. From the heats of formation of ethylene and butene-1 (25), \( \Delta H \) at 25°C, for the dimerization of ethylene is found to be -24.7 k.cal. \( \Delta H \) at 800° abs. was calculated, using the equation

\[ \Delta H = \Delta H_0 + \int_0^T \Delta C_p dT \]  

(2)
to be -26.5 k.cal. In this calculation it was again assumed that the difference in heat capacities arises mainly from the three translational and three rotational degrees of freedom which disappear when two molecules of ethylene are converted into a molecule of butene-1. It was also assumed that \( \Delta C_p \) remained constant over the temperature range involved.

The values for \( \Delta H^\circ \) and \( \Delta H \) give the heat of activation for the reaction

\[ C_4H_8(\text{butene}) = C_4H_8^\ast(\text{activated complex}) \]  

(10)
as approximately 58.4 k.cal. at 800° abs.

Although tetrafluoroethylene polymerizes readily to give the cyclic dimer, octafluorocyclobutane, in the case of ethylene, the corresponding reaction does not appear to occur under any experimental conditions. The occurrence of cyclobutane among the products of pyrolysis of ethylene was reported by Storch (102). This observation was held in some doubt, however,
and was not confirmed in a later paper (103). Other authors (8) report that cyclobutane is definitely not formed by pyrolysis of ethylene. Thus, since no experimental values are available, the heat of reaction for the dimerization of ethylene to cyclobutane has been calculated from the appropriate heat data.

The heat of combustion of cyclobutane has not been determined experimentally, but calculated values of 648 kcal. per mole, and 647.6 kcal. per mole have been quoted for $\Delta H_{\text{gas}}$ (104)(105). Using the former figure, a value of $-1.5$ kcal. is obtained for the heat of formation of cyclobutane gas at 25°C. Using this figure, and the heat of formation of ethylene at 25°C. (25), $\Delta H$ for the reaction

$$2\text{C}_2\text{H}_4 = \text{C}_4\text{H}_8(\text{cyclic})$$

is found to be $-26.5$ kcal.

In order to calculate the heat of reaction at 527°C. (ie. 800°C abs) the difference in heat content between two moles of ethylene and one mole of cyclobutane at 25°C and 527°C. must be known. Values for $C_p$ of ethylene are given in specific heat tables (25), but as the specific heat of cyclobutane has not been determined, values for $C_p$ of cyclobutane at 25°C and 527°C. were evaluated from the available data in the following manner.

At 527°C, the molar specific heat at constant volume of cyclopentane is 50.45 cal. per degree. Taking the contribution
of each of the translational and rotational degrees of freedom to the molar specific heat as $\frac{1}{2}R$ cal. per degree, it follows that the three translational and three rotational degrees of freedom provide 5.97 cal. per degree. The remaining 44.48 cal. per degree will be provided by the vibrational degrees of freedom, each of which contributes $R$ cal. per degree. In this way it is found that 57% of the total 39 vibrational degrees of freedom contribute to the molar specific heat of cyclopentane. By a similar calculation it was found that at 527°C, 61% of the vibrational degrees of freedom of cyclohexane contribute to the molar specific heat. On the assumption that 54% of the vibrational modes of cyclobutane contribute to the molar specific heat at 527°C, $C_p$ at this temperature was calculated to be 40.6 cal. per degree per mole. In a similar manner, $C_p$ at 25°C was found to be 15.6 cal. per degree per mole. Using these figures, and the values given for the molar specific heat of ethylene at 527°C and 25°C, $\Delta H$ for the reaction

$$2C_2H_4 = C_4H_8(cyclic)$$

was calculated, by means of equation (2), to be -24.8 k.cal. at 600°C absolute.

It has recently been reported that cyclobutane undergoes a homogeneous, first order decomposition at temperatures within the range 430°C to 480°C., ethylene being the sole product (106). The energy of activation of the reaction
\[
C_4H_8(\text{cyclic}) = 2C_2H_4 \tag{14}
\]

has been found to be approximately 61 k.cal. Using equation (8), a value of 59.5 k.cal. is obtained for \( \Delta H^\circ \) for the reaction (14), and combining this with the value of 24.8 k.cal. for \( \Delta H \) of reaction (13), the heat of activation of (13) is found to be approximately 34.7 k.cal. at 800° abs.

The heat and entropy data derived for the reactions of ethylene, butene-1, and cyclobutane are summarized in Table 15.

Table 15.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( E )</th>
<th>( P )</th>
<th>( \Delta H )</th>
<th>( \Delta H^\circ )</th>
<th>( \Delta S^\circ )</th>
<th>( \Delta S^\circ_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2C_2H_4 = C_4H_8(\text{butene}) )</td>
<td>35 k.cal.</td>
<td>( 5 \times 10^{-4} )</td>
<td>-26.5 k.cal. at 800° abs.</td>
<td>31.8 k.cal. at 800° abs.</td>
<td>-36.0 cal/° at 800° abs.</td>
<td>-13.5 cal/° at 800° abs.</td>
</tr>
<tr>
<td>( C_4H_8(\text{butene}) = 2C_2H_4 )</td>
<td>( \Delta H^\circ = 58.4 \text{ k.cal. at 800° abs.} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 2C_2H_4 = C_4H_8(\text{cyclic}) )</td>
<td>( \Delta H = -24.8 \text{ k.cal. at 800° abs.} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_4H_8(\text{cyclic}) = 2C_2H_4 )</td>
<td>( E = 61 \text{ k.cal.} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>( \Delta H^\circ = 34.2 \text{ k.cal. at 800° abs.} )</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>( \Delta H^\circ = 59.5 \text{ k.cal. at 800° abs.} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(ii) The dimerization of tetrafluoroethylene.

Tetrafluoroethylene dimerizes readily at temperatures in the region of 300° to 500°C. to give octafluorocyclobutane,

\[
2C_2F_4 = C_4F_8(\text{cyclic}) \tag{15}
\]

The energy of activation of this reaction has been found to be 25.4 k.cal. and a value of \( 3.85 \times 10^{-4} \) has been obtained for \( P \).
On substituting the value obtained for $\Delta S^\circ$ at 800° abs. into equation (7) (page 184), $\Delta S^\circ$ at 800° abs. is found to be -15.3 cal. per degree. This large negative value for the entropy of activation corresponds with the low figure for the probability factor and indicates that appreciable rearrangement of energy occurs among the various degrees of freedom when the activated complex is formed from two molecules of tetrafluoroethylene.

It is seen that the entropy of activation of the reaction

$$2\text{C}_2\text{H}_4 = \text{C}_4\text{H}_8(\text{butene})$$

(1)

is very similar to that of reaction (15). It is possible, therefore, that the activated complexes formed in the two reactions have similar configurations. The assumption made by Jahn (167) that the activated complex formed in reaction (1) has a butene-like structure seems justifiable, since values for the velocity constant of (1) calculated on the basis of this assumption, are in good agreement with those obtained experimentally. Hence, it is possible that the activated complex for reaction (15) will also have a structure resembling a butene.

It seems reasonable to assume that in the reaction

$$2\text{C}_2\text{H}_4 = \text{C}_4\text{H}_8(\text{cyclic})$$

(11)

the activated complex formed will have a similar structure to those formed in reactions (1) and (15). Hence, the probability factor and entropy of activation for reaction (11) should be of the same order as the values found for reactions (1) and (15).
The relative velocities of these three reactions should, therefore, depend largely on the magnitudes of their heats of activation. Thus, from the figures given in Tables 13 and 15, it is seen that whereas reactions (1) and (11) should have similar velocities, reaction (15) should, at any particular temperature, occur at a faster rate than either of these reactions.

It has been found experimentally that the quantity of tetrafluoroethylene which dimerizes in unit time is greater than the volume of ethylene which reacts in the same time and at the same temperature. This is as would be expected on the basis of the theory given above. Reaction (11), however, does not appear to occur at all, although theoretical calculations indicate that it should have a velocity similar to that of (1).

It has been shown experimentally (106), that cyclobutane decomposes readily at 450°C, to give principally ethylene. This indicates that cyclobutane is unstable at this temperature and accounts for the absence of cyclobutane from the products of pyrolysis of ethylene over the temperature range 300° to 500°C. It is possible, however, that at low temperatures the reaction

\[ 2\text{C}_2\text{H}_4 \rightleftharpoons \text{C}_4\text{H}_8(\text{cyclic}) \]  

may occur, and that the pyrolysis of ethylene at temperatures below 300°C, may yield appreciable quantities of cyclobutane.

The heat of activation for the reaction (15) is appreciably less than that calculated for the corresponding
reaction of ethylene. It has been shown (pages 61 et seq.) that the difference in the behaviour of ethylene and tetrafluoroethylene in certain reactions may be explained on the basis of the strong electron-attracting properties of the fluorine atoms in tetrafluoroethylene and the overlap of the \( \pi_p \) orbitals of the carbon atoms with the \( p \) orbitals of the fluorine atoms. The difference in the heats of activation of the dimerization reactions of ethylene and tetrafluoroethylene to give cyclobutane and octafluorocyclobutane respectively, may be accounted for in a similar manner.

In considering the activated complexes, it will be assumed that they have a butene-like structure, and that the end groups, i.e. \(-\text{CF}_2\) and \(-\text{CH}_2\), have similar configurations to those of the same groups in the molecules of tetrafluoroethylene and ethylene. In a \(-\text{CF}_2\) end group, as in the molecule of tetrafluoroethylene, there will be a certain amount of overlap of the two fluorine \( p \) orbitals with the \( \pi_p \) carbon orbitals in the same plane, and consequently a sharing of the five electrons in these orbitals between the three \( p \) orbitals. Three possible resonance hybrid structures can result from this sharing of electrons, and these are shown in Figure 39. The dots inside each orbital represent the number of electrons in that orbital. In the activated complex formed from ethylene, there will be little, if any, sharing of the electrons in the hydrogen \( s \) and
carbon up orbitals since these orbitals are of different symmetry types.

\[ \text{(i)} \quad \text{As since these orbitals are of different symmetry types.} \]

\[ \text{(ii)} \quad \text{tr.} \]

\[ \text{(iii)} \quad \text{tr.} \]

**Figure 39.**

As a result of the occurrence of hybrid structures of the type shown above, the \( \text{C}_4\text{F}_8^+ \) activated complex will have a certain amount of resonance energy not possessed by the \( \text{C}_4\text{H}_8^+ \) activated complex. This resonance energy will result in a lowering of the energy barrier over which the reacting tetrafluoroethylene molecules must pass, and consequently a lowering of the heat of activation of the reaction

\[ 2\text{C}_2\text{F}_4 = \text{C}_4\text{F}_8(\text{cyclic}) \quad (15) \]

This may account in part, for the difference between the heat of activation of reaction (15) and that of the reaction

\[ 2\text{C}_2\text{H}_4 = \text{C}_4\text{H}_8(\text{cyclic}) \quad (11) \]

(iii) The thermal decomposition of octafluorocyclobutane.

Octafluorocyclobutane decomposes slowly in the region of 500° to 600°C, to give tetrafluoroethylene,

\[ \text{C}_4\text{F}_8(\text{cyclic}) = 2\text{C}_2\text{F}_4 \quad (17) \]

The energy of activation of reaction (17) has been found to be
74.1 kcal., and the A factor in the equation
\[ k = Ae^{-E/RT} \] (18)
has a value of \(8.9 \times 10^{15}\) sec\(^{-1}\).

In a large number of unimolecular reactions the A factor has a value of the order of \(10^{13}\) to \(10^{14}\) sec\(^{-1}\). The observed specific rates for a number of unimolecular gas reactions, however, give A factors which are several powers of 10 greater than the normal value. The reaction (17) may clearly be included among these abnormal reactions. In general, reactions which involve ring opening tend to have high A factors. Thus, for the decomposition of cyclopropane, \(A = 1.48 \times 10^{15}\) sec\(^{-1}\) and for the decomposition of trioxymethylene \(A = 1.43 \times 10^{16}\) sec\(^{-1}\).

According to the absolute reaction rate theory, the specific rate constant for a unimolecular reaction is given by
\[ k = \frac{e^{k \frac{T}{h}} e^{-E/RT}}{\frac{\Delta S^f}{R}} \] (19)
On comparing this equation with equation (18) it is seen that for the simple collision theory to be obeyed, the relationship
\[ A = e^{k \frac{T}{h}} e^{\frac{\Delta S^f}{R}} \] (20)
must be applicable. As mentioned above, \(A\) is normally of the order of \(10^{14}\) sec\(^{-1}\) and since \(e^{k \frac{T}{h}}\) is approximately \(2 \times 10^{13}\), \(\Delta S^f\), which for a unimolecular reaction is independent of the standard state, should be of the order of 3 calories per degree. Thus in the decomposition of acetone, \(A = 1.6 \times 10^{13}\) sec\(^{-1}\) and \(\Delta S^f\) is 2.5 cal. per degree. Similarly for the decomposition of
silicon tetramethyl $A = 1.7 \times 10^{14} \text{ sec}^{-1}$ and $\Delta S^*$ is 2.2 cal. per degree. It is seen from equation (20) that for the reactions which have high $A$ factors we should expect a correspondingly high value for the entropy of activation, and this is found in practice. Thus, in the decomposition of azomethane, for which $A = 8.0 \times 10^{15} \text{ sec}^{-1}$, $\Delta S^*$ is 10.8 cal. per degree. For the reaction

$$\text{C}_4\text{F}_8(\text{cyclic}) = 2\text{C}_2\text{F}_4$$  \hspace{1cm} (17)

$A = 8.9 \times 10^{15} \text{ sec}^{-1}$ and $\Delta S^*$ is found to be 10.6 cal. per degree.

Other reactions which involve the breaking of a ring also have a large entropy of activation. The values of $\Delta S^*$ for the decomposition of ethylene oxide and trioxymethylene are 7.5 and 17.5 cal. per degree, respectively.

It is easier in discussing these 'abnormal' reactions to consider the meaning of the observed entropy changes, since the general significance of changes in entropy is understood. In general, the activated complex formed in a unimolecular reaction will have a looser structure than that of the reactant molecule, hence, there will be a greater freedom of motion in the activated state. The formation of the activated complex is then accompanied by an increase of entropy.

In the unimolecular reaction (17) the entropy of activation is unusually high. It has been shown earlier (page 189) that the activated complex formed in the dimerization of tetrafluoro-
Figure 4.0

Structure proposed for activated complex
ethylene probably has a butene-like structure. The high value for the entropy of activation of (17) supports this theory, since it is unlikely that a mere loosening of the octafluorocyclobutane ring would give rise to such a large increase in entropy. The rupture of one of the C-C bonds in octafluorocyclobutane would, however, result in a large increase in the freedom of motion, and hence, lead to a high value for $\Delta S^\circ$. A rough calculation of the entropy change which will occur when an activated complex with a butene-like structure is formed from a molecule of octafluorocyclobutane is given below.

In order to evaluate the increase in entropy when a molecule of octafluorocyclobutane is converted into the activated complex, a structure for this complex must be postulated. The structure shown in Figure 40 has been assumed for the purpose of the calculation. The carbon atoms $C_1$ and $C_4$ have been assumed to have $sp_2$ hybrid structures, whilst $C_2$ and $C_3$ have been assumed to have $sp_3$ hybrid structures. The bond lengths have been proposed by analogy with the lengths of similar bonds in tetrafluoroethylene and octafluorocyclobutane.

In the structure shown in Figure 40, free rotations about the bonds $C_1-C_2$, $C_2-C_3$, and $C_3-C_4$ may occur. The contributions of these free internal rotations to the entropy of the activated complex may be calculated using the following equation (108)

$$S_{i.r.}^0 = 2.287(\log_{10}T + \log_{10}I_m - 2\log_{10}n) + 89.93$$
In this equation \( n \) is the number of indistinguishable positions of the rotating group, and \( I_m \) is its "reduced" moment of inertia. The latter is given by

\[
I_m = I_m^0 \left\{ 1 - I_m^0 \left( \frac{\lambda_x}{I_x} + \frac{\lambda_y}{I_y} + \frac{\lambda_z}{I_z} \right) \right\}
\]

where \( I_m^0 \) is the moment of inertia of the rotating group about the axis of rotation, \( \lambda_x \) is the cosine of the angle between the axis of rotation and the axis of the moment of inertia \( I_x \) of the whole molecule, and similarly for \( \lambda_y \) and \( \lambda_z \). In calculating the moments of inertia of the structure shown in Figure 40, the axes have been taken as indicated in the figure.

For the internal rotation about the bond \( \text{C}_2\text{C}_3 \), \( I_m = \frac{I_x}{4} = 190.0 \times 10^{-40} \) and \( n=1 \), hence at 800° abs.

\[
S_{f.i.r.} = 2.287(\log_{10} 800 + \log_{10} 190 \times 10^{-40}) + 89.93
\]

\[= 10.3 \text{ cal. per degree}.\]

For the internal rotations about the bonds \( \text{C}_1\text{C}_2 \) and \( \text{C}_3\text{C}_4 \)

\[
I_m = I_m^0 \left\{ 1 - I_m^0 \left( \frac{\cos^2 71^0}{I_x} + \frac{\cos^2 19^0}{I_y} + \frac{\cos^2 290^0}{I_z} \right) \right\}
\]

\[= 52.9 \times 10^{-40} \]

and \( n = 2 \). Thus at 800° abs.

\[
S_{f.i.r.} = 2.287(\log_{10} 800 + \log_{10} 52.9 \times 10^{-40} - 2\log_{10} 2) + 89.93
\]

\[= 7.5 \text{ cal. per degree}.\]

Thus the three free internal rotations will contribute 25.3 cal. per degree to the entropy of the activated complex.

These internal rotations will replace three vibration frequencies of the octafluorocyclobutane molecule. From the
vibration spectra data for octafluorocyclobutane given by Cleasen (90) the lowest frequency, which has been assigned to out-of-plane ring bending, has a wave number of 86 cm\(^{-1}\). There should be two such vibrations of this type and at 800\(^0\) abs. they will contribute 11.7 cal. per degree to the entropy of octafluorocyclobutane. The next smallest vibration frequency, corresponding to CF\(_2\) twisting, has a wave number of 173 cm\(^{-1}\) and will contribute 4.1 cal. per degree to the entropy of the molecule at 800\(^0\) abs. The contribution of the three lowest vibrations to the entropy of octafluorocyclobutane is, therefore, 15.8 cal. per degree. The minimum possible value of the increase in entropy on the formation of the activated complex will be the difference between this figure and the entropy contribution of the three internal rotations, i.e. 9.5 cal. per degree. The average entropy contribution of a vibration frequency to the entropy of a molecule of octafluorocyclobutane has been calculated to be approximately 3 cal. per degree at 800\(^0\) abs. Thus, on average, the loss of three vibration frequencies will result in a decrease of 9 cal. per degree in the entropy of the molecule, and the increase in entropy on the formation of the activated complex will be approximately 16 cal. per degree. The activated complex will have one vibrational degree of freedom less than the molecule of octafluorocyclobutane and hence this calculated figure may be a little high. It is, however, sufficiently close
to the experimental figure to justify the assumptions made regarding the structure of the activated complex.

From the above discussion it appears that the energy of activation for the reaction

\[ \text{C}_4\text{F}_8(\text{cyclic}) = 2\text{C}_2\text{F}_4 \quad (17) \]

should be approximately equal to the energy of a C\text{-}C bond, since the formation of an activated complex involves only the rupture of this bond. The experimental value of 72.6 k. cal. obtained for the heat of activation is somewhat less than the figure normally taken for the C\text{-}C bond strength. The difference may be attributed in part to the extra energy of the activated complex, acquired by resonance between structures of the type described on page 191. Thus, it is seen that the experimental values obtained for the entropy and heat of activation of reaction (17) can be satisfactorily accounted for by assuming that the activated complex has a butene\text{-}like structure.

Since the activated complex formed in the decomposition of cyclobutane will not possess the resonance energy of the octafluorocyclobutane complex, the heat of activation for the reaction

\[ \text{C}_4\text{H}_8(\text{cyclic}) = 2\text{C}_2\text{H}_4 \quad (18) \]

might be expected to be greater than the value obtained for the corresponding reaction of octafluorocyclobutane. The experimental
value obtained for the heat of activation of (18), i.e. 59.5 k.cal. is, in fact, less than that obtained for (17). It has been pointed out that spectroscopic evidence favours a planar ring in cyclobutane, whereas in the case of octafluorocyclobutane spectral and electron diffraction data favour a non-planar carbon ring. This distortion of the carbon ring in octafluorocyclobutane has been attributed to the repulsive forces between carbon atoms attached to different carbon atoms. These repulsive forces favour ring opening. Thus, according to the picture given above, in comparison with reaction (18), reaction (17) is aided both by a resonance effect in the activated complex and a repulsion effect in the ground state. The fact that reaction (17) has the higher activation energy means that there is a third effect countering the two effects mentioned. The nature of this third effect will be discussed below.

(iv) The equilibrium reaction \(2C_2F_4 \leftrightarrow C_4F_8(cyclic)\)

From the experimental data obtained, \(\Delta H\) and \(\Delta S\) for the reaction

\[
2C_2F_4 \leftrightarrow C_4F_8(cyclic) \quad (19)
\]

have been calculated to be -50.3 k.cal. and -49.2 cal. per degree respectively, at 800° abs. From thermochemical data, \(\Delta H\) for the reaction

\[
2C_2H_4 \leftrightarrow C_4H_8(cyclic) \quad (16)
\]

has been estimated to be -24.8 k.cal. at 800° abs. As the
cyclobutanes contain twelve bonds and the reacting olefine molecules ten bonds, the difference between this figure and that obtained for reaction \(19\) does not necessarily indicate any great structural differences between the fluorocarbons and the hydrocarbons involved.

The translational plus rotational entropies of two molecules of tetrafluoroethylene and one molecule of octafluorocyclobutane have been evaluated using the equations (108)

\[
S_T^0 = 2.287(5\log_{10} T + 3\log_{10} M) - 2.314
\]

and

\[
S_R^0 = 2.287(3\log_{10} T + \log_{10} I_x I_y I_z - 2\log_{10} c) + 267.5
\]

and found to be 142.6 cal. per degree and 77.9 cal. per degree, respectively, at 800\(^\circ\) abs. Since the entropy change for reaction \(19\) is 49.2 cal. per degree at 800\(^\circ\) abs., the contribution of the 30 vibrational degrees of freedom of octafluorocyclobutane to the entropy of the molecule must exceed that of the 24 vibrational degrees of freedom of two molecules of tetrafluoroethylene by 15.5 cal. per degree. Using the equation

\[
S_{Vib.}^0 = \frac{R \lambda}{c^x - 1} - R \log_e (1 - e^{-x})
\]

where \(x = \frac{h \lambda^2}{kT}\), and \(\lambda\) = the fundamental vibration frequency, several of the very low vibrational frequencies in octafluorocyclobutane have been calculated to contribute the unusually high figure of 4 to 6 cal. per degree each, towards the entropy of the molecule at 800\(^\circ\) abs. The lowest frequency vibrations in octafluorocyclobutane are associated with the ring structure.
and no corresponding vibrations occur in tetrafluoroethylene.

A comparison of the heats of activation of the reactions (17) and (18) and the heats of reaction for (19) and (16) indicate that there is a source of stability in octafluorocyclobutane not present in cyclobutane. It is difficult to decide the cause of this stability, since octafluorocyclobutane is a molecule in which the concept of independent locational bonds breaks down seriously. The following complications will arise due to the presence of fluorine atoms in the molecule.

(i) The high electronegativity of the fluorine atom will give rise to appreciable ionic effects in the molecule of octafluorocyclobutane which will not occur in cyclobutane.

(ii) Conjugation effects similar to those in carbon tetrafluoride and tetrafluoroethylene must be present. This implies that the fluorine 5p electrons in octafluorocyclobutane contribute to the bonding in the molecule.

(iii) The possibility of resonance of the type mentioned on page 191 introduces an important difference between the reactions of octafluorocyclobutane and cyclobutane.

(iv) The repulsive forces between fluorine atoms attached to different carbon atoms must have an appreciable effect on the strengths of the C-F and C-C bonds in octafluorocyclobutane.

The relative magnitudes of these effects in the molecules of tetrafluoroethylene and octafluorocyclobutane cannot be
assessed, and hence, any examinations of the molecules on the basis of a simple theory is extremely difficult.

A comparison of bond lengths in the molecules under consideration is of little assistance, since no data are available for the lengths of the C-C and C-H bonds in cyclobutane. Values quoted for the C=C bond lengths in tetrafluoroethylene and ethylene indicate that the bond is slightly longer in the latter molecule (109)(110), suggesting that the C=C bond in ethylene is weaker than in tetrafluoroethylene. This would lead to a smaller heat of reaction for (19) than for (16). Thus for the heat of reaction of (19) to be greater than that of (16) the C-C bonds in octafluorocyclobutane must be stronger than the corresponding bonds in cyclobutane, assuming that the strengths of the C-F and C-H bonds are the same in the respective cyclic and unsaturated fluoro- and hydrocarbons.

(v) Direction of future work.

The work described in Part II of this thesis constitutes a qualitative investigation of the reactions occurring when tetrafluoroethylene is heated at various temperatures between 300°C and 800°C. This investigation has provided useful information on which to base further quantitative studies. The work described in Part III of the thesis represents the first step in these quantitative studies, namely, the investigation of the kinetics of the reactions occurring at the lower temperatures.
Two interesting problems arise from the qualitative results obtained for the reactions occurring at temperatures above 600° C.

(i) The mode of formation of hexafluoropropene.

(ii) The mode of formation of the low molecular weight saturated and high molecular weight unsaturated products of pyrolysis of tetrafluoroethylene at 800° C.

As the reactions occurring at temperatures above 600° C. will be fast, it will probably be impracticable to attempt to follow the reactions occurring by the rate of change of pressure in the reaction vessel. The practical work involved in the investigation of (i) will, therefore, involve the analysis of the products of pyrolysis of tetrafluoroethylene at temperatures between 600° and 700° C. after various reaction times.

With regard to (ii), the investigation of the free radical mechanisms proposed would involve the heating of octafluorobutene-1 at 800° C. in a flow system, in the presence of a carrier gas such as toluene. The presence of free radicals in the system would be shown by the formation of trifluoromethane.

From the theoretical discussion of the thermal reactions of ethylene, it appears that at low temperatures the gas should dimerize to give cyclobutane. The fact that this compound has not been found among the products of pyrolysis of ethylene may be due to the instability of cyclobutane at the temperatures at which the thermal decomposition of ethylene has been investigated.
It would, therefore, be interesting to examine the products of pyrolysis of ethylene at temperatures below 300°C., as it seems likely that under sufficiently mild conditions appreciable quantities of cyclobutane should be formed.

Further work which should prove of interest is the study of the thermal reactions of hexafluoropropene and higher olefines. At first sight it appears probable that hexafluoropropene will dimerize to give a substituted octafluorocyclobutane, and an investigation of this reaction should provide an interesting comparison with the corresponding reaction of tetrafluoroethylene.
Appendix.

The kinetics of the dimerization of tetrafluoroethylene, chlorotrifluoroethylene and of their interdimerization has recently been studied by Lacher, Tompkin, and Park (111). The dimerization of tetrafluoroethylene was studied at temperatures between 288° and 466°C. It was found that the values obtained for the velocity constant could be represented by the equation

\[ k = 16.5 \times 10^{10} \exp\left(-\frac{26.299}{RT}\right) \text{ cc./mole sec}^{-1}. \]

The corresponding equation obtained from the results given in this thesis is

\[ k = 10.3 \times 10^{10} \exp\left(-\frac{25.400}{RT}\right) \text{ cc./mole sec}^{-1}. \]

There is seen to be reasonable agreement between the numerical constants in the two equations.

It was pointed out that the ratios of the Arrhenius "A-factors" for any two of the reactions

\[ 2C_2F_4 = C_4F_8(cyclic) \]
\[ C_2F_4 + C_2F_3Cl = C_4F_7Cl(cyclic) \]
\[ 2C_2F_3Cl = C_4F_6Cl(cyclic) \]

depended mainly on the values for the symmetry numbers of the reactants and activated complexes. By assuming that the latter had configurations similar to those of the cyclic products, it was found that the experimental data could best be represented by assuming that octafluorocyclobutane had a puckered ring rather than a planar ring.
The experimental results obtained from the work described in this thesis suggest that the activated complex formed in the dimerization of tetrafluoroethylene has a butene-like structure rather than a cyclic structure. Values for the ratios of the "A-factors" have been calculated on the basis of the assumption that the activated complexes formed in the above three reactions have butene-like structures. On the basis of this assumption a large number of possible values for the ratios of the "A-factors" may be obtained. It has been found that in some cases the calculated values correspond to those obtained from the experimental results of Lacher, Tompkin, and Park. The experimental results of the above authors can, therefore, be accounted for equally well by assuming that the activated complexes have a butene-like structure as by assuming that they have a cyclic structure.
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