PERFLUOROCARBONS IN ELECTRICAL DISCHARGES

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SUMMARY

The use of perfluorocarbon fluids as electrical insulants focuses attention on the need for a better understanding of the behaviour of electronegative materials when subjected to electrical stress and discharge conditions.

Electron affinity can play an important role, and its measurement for several perfluorocarbon and sulphur compounds by the magnetron method is described.

The degradation chemistry of a range of perfluorocarbon compounds subjected to thermal and non-thermal discharge is investigated. Substantially different product compositions are obtained in the two discharge regimes and are analysed in terms of the structure of the parent compounds. The nature of the scission and product formation processes is deduced.

PREFACE

This dissertation, which is being submitted for the degree of Doctor of Philosophy in the University of Aston in Birmingham, is an account of work carried out from September 1967 to September 1970 under the supervision of Professor F.M. Page Ph.D., Sc.D. in the Department of Chemistry of the University of Aston in Birmingham and with the co-operation of the Imperial Smelting Corporation and the Central Electricity Generating Board. Dr. G. Fuller of the Imperial Smelting Corporation and Mrs. R. Redfern of the Central Electricity Generating Board acted as industrial supervisors.

I wish to express my gratitude to Prof. F.M. Page, Dr. G. Fuller, and Mrs. R. Redfern for their guidance and encouragement, and to the Science Research Council for the provision of a Research Studentship under the C.A.P.S. scheme.

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1. INTRODUCTION

Perfluorocarbons are compounds analogous to hydrocarbons from which in general they are prepared by the replacement of all hydrogen atoms by fluorine atoms. The effect of this replacement is considerable in terms of both chemical and physical properties.

Perfluorocarbons are in general more stable chemically than hydrocarbons. Resistance towards chemical attack is attributable in part to the greater steric shielding of the carbon atom skeleton by the fluorine atoms. The carbon-fluorine bond is also appreciably stronger than the carbon-hydrogen bond. Considerably higher temperatures are generally required to produce thermal degradation of a perfluorocarbon.

A remarkable physical property of perfluorocarbons is their weak intermolecular attraction exhibiting itself in high volatility and low surface tension relative to hydrocarbons.

Hydrocarbons have been widely used for many years as insulating materials in electrical equipment, particularly transformer housings. Their heat transfer properties are poor, they are flammable, and they are incompatible with some construction materials. Nevertheless hydrocarbon transformer oils have a reasonable electrical strength and are relatively inexpensive. Perfluorocarbons by contrast, have excellent heat transfer properties, are thermally more stable, are non-flammable, and are compatible with most construction materials, in addition to having a very high electrical strength. The ability of perfluorocarbon fluids to dissipate large heat fluxes is of particular importance. A combined insulant-coolant role is frequently valuable in electrical equipment. The substitution of perfluorocarbons for hydrocarbons in this role often allows considerable reduction in size and weight. Denser packing of microcircuits and silicon rectifiers with operation at higher power levels can be readily achieved by immersion in a perfluorocarbon fluid. The elimination of very localized microcircuit hot spots by this method is particularly useful. Perfluorocarbons are therefore finding increasing application in sophisticated high power electronic equipment as insulants and coolants when their higher cost is not a prime consideration.

Commercial utilization of perfluorocarbons has focused some attention on the need for a better understanding of their electrical behaviour. Central to an understanding of the electrical strength of perfluorocarbon fluids is a knowledge of their electron affinity. Capture of electrons inhibits the electron multiplication processes which precede electrical breakdown. The measurement of the electron affinity of several compounds was carried out and is described in the first part of this dissertation.

In common with all insulating materials, electrical discharge and breakdown conditions can be induced in perfluorocarbons by the application of sufficient electrical stress. Electrical discharge and breakdown are accompanied by chemical reaction. The chemical behaviour of perfluorocarbons subjected to electrical discharge has not previously been studied extensively but is of great practical importance as well as being of interest in its own right. Many perfluorocarbons were therefore subjected to electrical discharges and the reaction products examined. The second and major part of this dissertation describes this work.

PART I

ELECTRON AFFINITY

2. PRELIMINARY CONSIDERATIONS CONCERNING ELECTRON AFFINITY AND ITS ESTIMATION

2.1 The effect of electron attachment on the electrical conductivity and breakdown of dielectric liquids and gases.

Electrical conductivity and breakdown phenomena in dielectric liquids and gases have been extensively studied (1) (2).

A great number of fundamental physical phenomena have been observed when an electric field is applied across a dielectric medium. The complexity of these phenomena has precluded the formulation of a unified theoretical treatment which can give a full explanation of all the known experimental facts (1). A number of conflicting theories have current partial acceptance. The physical processes which occur cannot therefore be considered well understood. The attendant chemical processes have been less well studied and are even less well understood.

Within these limitations the mechanisms of conduction and breakdown in liquids and gases are normally considered to be broadly similar.

Cosmic radiation ionizes a small number of molecules in the dielectric medium producing a residual self-conductivity, so that, for example, even the purest dielectric liquids have a conductivity of $10^{-19} - 10^{-20}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. When an electric field is applied across the medium these ions will be drawn towards electrodes of opposite polarity, giving rise to an electric current. This ionization current increases with applied voltage until a saturation current is reached when the applied voltage is sufficient to enable collection of all charges in the medium. At lower applied voltages the transit time of the ions is sufficiently long for recombination to remove a fraction of them so that a lower current flows. As progressively higher voltages are applied the saturation current is not exceeded until a point is reached at which increased voltage causes an exponential rise in the current, eventually producing breakdown. At such applied voltages, the logarithm of the current is proportional to the electrode separation at a given field strength, indicating that a multiplication of charges is occurring. Between collisions, some electrons acquire sufficient velocity from the applied field to produce collision ionization of other molecules. This produces more electrons, so that at sufficiently high applied voltages a cascade electron multiplication process causes the number of charges to become virtually infinite, with the formation of a highly conductive path between the electrodes. This is electrical breakdown.

Electronegative substances have an affinity for free electrons with which they form negative ions. If a dielectric medium contains electronegative substances, then attachment of electrons to form negative ions will reduce the number of free electrons. The negative ions have a considerably greater mass than the free electrons and cannot therefore acquire sufficient momentum from the applied field to cause collision ionization of other molecules. Depending upon the effectiveness of the electronegative substance in attaching electrons, the electron multiplication process is therefore inhibited and much higher applied voltages are then necessary to produce breakdown than in the absence of the electron attaching substance. This effect, produced by sulphur hexafluoride (3) and oxygen (4), has been well studied.

Electron attachment by electronegative substances is of major practical importance in its application to high voltage insulation. Sulphur hexafluoride and perfluorocarbon compounds are strongly electronegative and have become commercially important as insulating materials in high voltage equipment where a particularly high insulating efficiency is necessary.

2.2 The determination of electron affinities.

The electron affinity of a species is a convenient description of the stability of the negative ion that it forms by combination with an electron. When an electron and the isolated species come together from an infinite separation to form a stable combination, the decrease in energy of the system is defined as the electron affinity of the parent species. The parent species concerned is usually a neutral atom, radical or molecule.

2.2.1 Theoretical approaches to the estimation of electron affinities.

The electron affinity of a species depends on its electronic configuration and polarizability. A consideration of these factors can therefore lead to the prediction of electron affinities.

Negative ions can be conveniently classified into four groups(5):

(i) Ions formed when a free radical accepts an electron to form a singlet ion. The electron is apparently localized in a lone pair.

In this case the electron affinity of the radical is similar to that of the acceptor atom in the same valence state, unless fluorine is present. Hinze (6) and later Hinze & Jaffe(7)(8) evaluated the electronegativities of elements in their valence states by quantum mechanical calculation of promotion energies from the spectroscopic ground state to the valence state, followed by the extrapolation of these values to negative ions by Rohrlich's method(9). The valence state of the electron acceptor and of the ion formed are determined by their structure, geometry and energy.

Combination of the atomic electron affinity with the promotion energies corresponding to the chosen valence states then allows prediction of the electron affinity of the free radical acceptor. Reasonably reliable estimates(5) of atomic electron affinities are readily available. Gaines & Page(10) and Page & Goode(5) have applied the method of Hinze & Jaffe to the hydrides of all elements for which valence state promotion energies were available.

(ii) Negative ions formed from singlet molecules having a delocalized π electron system. The energy of the lowest unoccupied orbital will be strongly dependant on the internal electrostatic field and is readily amenable to calculation. Farragher & Page(11) have analysed the relation between polar substituent groups and the direct capture affinity of a number of π-delocalized molecules.

(iii) Doublet ions formed when singlet molecules without delocalized π-systems capture an electron. Estimation of the polarization of the molecule allows prediction of the electron affinity. Page & Goode(5) have used this approach to predict the electron affinities of a number of such molecules and have compared these predictions with experimental values.

(iv) Negative ions formed from multiplet acceptors such as S^- and O^-.

Most of the ions of interest in the first three groups are polyatomic and their complex nature allows only a rough estimate of their stability to be obtained by application of the methods described above. More exacting calculations have been possible for monatomic and diatomic species, giving results often in excellent agreement with the best experimental determinations. Most of these calculations have involved sophisticated estimates of lattice energies and application of the Born-Haber cycle. Alkali halides(12)(13), hydrides(14), oxides(15), hydroxides(17), cyanides(18), nitrites(19), nitrates(19), amines(20), and alkaline earth oxides and sulphides(16) have been subjected to this approach.

Glockler(22) related electron affinity to atomic number and known ionization potentials of isoelectronic species. Edlèn(23) improved this method by introducing corrections to allow for electronic screening effects. For many atoms this method gives good agreement with experimental values.

Quantum mechanical calculations have been used successfully for the simplest atomic species. Thus Pekeris(24) has estimated the electron affinity of H, and Wu(25) has estimated the electron affinity of He and Li. Clementi et al(26) have used Hartree-Fock approximations to calculate the electron affinities of larger atoms up to Cl.

Theoretical approaches have been capable of giving accurate estimates of the electron affinities of monatomic and a few diatomic species. But with increasing atomic number and with polyatomic species it is necessary to introduce increasingly crude approximations giving results that are often not in very satisfactory agreement with experiment.

2.2.2 The experimental determination of electron affinities.

Experimental methods involve either a measurement of the energy required to attach or detach an electron, or studies of equilibria between electrons, molecules and ions.

Of the former type of approach are the photodetachment studies of Branscomb et al(28) and Berry et al(29). These have given particularly accurate results by virtue of the spectroscopic nature of the method. Branscomb et al generated negative ions in a discharge; after mass filtering, the ions were subjected to a beam of monochromatic light whose frequency was varied until it was just sufficient to detach electrons. Berry et al used the shock tube as a means of generating negative ions. In both cases the method is limited principally to halide ions since only these can be produced in sufficient concentration.

Attachment methods are generally mass spectrometric using mono-energetic electron impact(30). Measurement of the appearance potential of a negative ion in a mass spectrometer can give a lower limit on the electron affinity, but actual determination depends on the development of methods to measure the kinetic energies and vibrational excitation(31) associated with ion formation.

Equilibrium studies generally require elevated temperatures and are therefore carried out in flames or at hot metal surfaces.

Rolla & Picardi(32) heated a metal filament in a flame to produce electrons which were collected by a metal plate at a positive potential. The presence of an electron-attaching substance in the flame reduced the electron current enabling calculation of the electron affinity. However, only strongly electronegative, thermally stable substances could be used and there are considerable uncertainties due to the complex nature of flame chemistry.

Dukel'skii & Ionov(33) studied the equilibrium set up when beams of alkali halide molecules dissociated to positive and negative ions on a hot tungsten filament. The positive and negative ion currents measured were related to the electron affinity of the halide atom by the Saha-Langmuir equation.

The methods described above are restricted to a very few simple species. An equilibrium method of application to a wider range of complex species is the electron capture method of Becker & Wentworth(34). A plasma of secondary electrons and positive ions is produced in a cell through which a carrier gas flows. A voltage pulse collects and measures the electrons. In the presence of an electron-accepting substance the electron current is reduced. Assuming equilibrium, the electron affinity of this substance can be determined by statistical calculation, or by second law methods if measurements are made at several temperatures. Many aromatic hydrocarbons have been studied in this way. There are uncertainties however in that the chemistry may be more complex than envisaged.

The method which has been most extensively applied to the measurement of the stability of both simple and complex negative ions is the

Magnetron technique of Sutton & Meyer(35) further developed by Page, Farragher, and co-workers(5).

A hot filament at a negative potential thermionically emits electrons which are collected by a concentric anode. The presence between the filament and the anode of a concentric double squirrel cage grid at an intermediate potential causes the electrons to follow helical paths and be captured by the grid when a strong magnetic field from a surrounding solenoid is applied. The heavier negative ions are unaffected and can then be separately collected at the anode. The knowledge of the substrate, electron and negative ion concentrations at various temperatures then allows calculation of the free energy change from which under suitable circumstances the electron affinity can be deduced. A disadvantage of the method is that a simple reaction behaviour of the substrate at the filament is necessary, as this and the identity of the negative ion formed can only be deduced by indirect means, namely by consideration of the energies involved. Some progress towards overcoming the problem of ion identification has been made by coupling the magnetron to a quadrupole mass spectrometer(36) and this is being further extended(40).

Page(37) chose the magnetron technique as a general method of determination of electron affinities. An extensive study has been made by Page, Farragher(38), Burdett(39), Goode(36), and other workers of the stabilities of many negative ions and the results obtained have often been in good agreement with those obtained by other methods.

The magnetron method was therefore used in the study of the stability of negative ions formed by some sulphur compounds and some fluorocarbon compounds related to materials of commercial importance as electrical insulating fluids.

3 THE MAGNETRON METHOD

3.1 The theory of the magnetron(41)

Figure 1 shows the forces acting upon an electron emitted from the hot central filament of a diode placed in a uniform magnetic field, of flux density B, running parallel to the length of the filament.

The electrostatic and electromagnetic forces acting upon the electron are respectively

$$F = -eE = -e \frac{dV}{dr}$$

and $f = Bev$ where e is the electron charge, V is the potential at a distance r from the filament and v is the velocity of the electron at this point. If v is resolved into components v_r and v_θ along and perpendicular to the radius vector, then the components of f will be

$$f_r = Bev_\theta \quad \text{and} \quad f_\theta = Bev_r$$

If θ is the angle between the radius vector and an arbitary line in the azimuthal plane, the angular velocity of the electron is

$$\omega = \frac{d\theta}{dt} = \frac{v_\theta}{r}$$

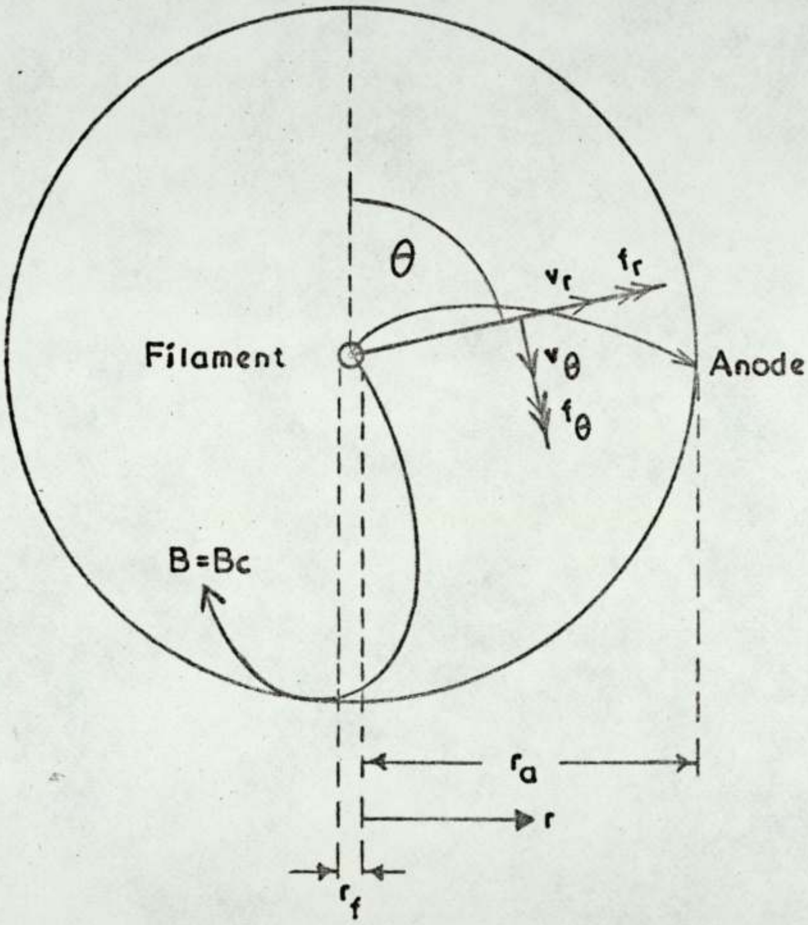


FIGURE 1

The forces acting upon an electron

The equation of radial motion therefore becomes

$$\frac{d}{dt}\left(m\,\frac{dr}{dt}\right) = F - f_r = e\,\frac{dV}{dr} - Ber\,\frac{d\theta}{dt} \qquad (1)$$

where m is the mass of the electron.

The equation of azimuthal motion is found by equating the moment of the impressed force to the rate of change of the angular momentum, thus:-

$$rf_{\theta} = rBe\,\frac{dr}{dt} = \frac{d}{dt}\,(mr^2\omega)$$

Integrating each side with respect to time, and noting that $\omega = 0$ as the electron leaves the filament, gives:

$$\omega = \frac{Be}{2m}\left(1 - \frac{r_f^2}{r^2}\right) \qquad (2)$$

If the small thermal velocity with which the electron leaves the filament is ignored, its velocity at a point at which its potential is V will be given by

$$v = \sqrt{\frac{2e}{m}V}$$

$$= \left[\left(\frac{dr}{dt}\right)^2 + r^2\left(\frac{d\theta}{dt}\right)^2\right]^{\frac{1}{2}} \cancel{+\left(\frac{dz}{dt}\right)^2\Big]^{\frac{1}{2}}}$$

(Considering motion in the azimuthal plane only)

At a certain value of the magnetic field strength, $B = Bc$, the electron will just fail to reach the anode.

At this point

$$V = V_a$$

$$\frac{dr}{dt} = \frac{dz}{dt} = 0$$

$$r = r_a$$

$$\frac{d_\theta}{dt} = \omega$$

whence

$$\omega = \frac{v_\theta}{r_a}$$

$$= \frac{1}{r_a} \sqrt{\frac{2e}{m} V_a} \qquad (3)$$

Therefore equating (2) and (3)

$$B_c = \frac{\sqrt{8V_a}}{r_a \left[1 - \left(\frac{r_f^2}{r_a^2}\right)\right] \sqrt{e/m}} \qquad (4)$$

whence if $r_a >> r_f$

$$B_c = \sqrt{\frac{8mV_a}{er_a^2}} \qquad (5)$$

Equation (4) shows the value of B_c to be independent of the potential distribution between the anode and the cathode so that the presence of other electrodes or space charge effects should not alter the cut-off conditions. In practice the cut-off is not so sharp with grids present, probably because of distortion of the magnetic and electric fields by these structures. The efficiency of removal of electrons is however much higher. In the magnetron tetrode, two grids at potentials lower than that of the anode collect the electrons so preventing the creation near the filament of a space charge which would affect the emission of negative ions. The magnetic field strength is usually made greater than B_c so that the apogee occurs near the inner grid, allowing a greater efficiency of electron removal. Page(37) showed that the presence of a second grid further increases the efficiency of electron collection, presumably because of its action in trapping electrons which had passed through the first grid because of potential and geometric asymmetry within the apparatus.

3.2 Design of the apparatus.

A magnetron assembly was constructed on a 0.25 in. thick brass plate as in Figure 2. This fitted by means of a rubber O-ring to the ground glass top edge of a 10 in. long 4 in. diameter section of Quickfit and Quartz pipeline tube which was in turn mounted on a Genevac diffusion pump as in Figure 3. This arrangement allowed ready access to the magnetron assembly for cleaning and repair.

Electrical connections through the brass plate acted as supports for the magnetron assembly and were made using metal-to-glass seals soldered into holes drilled in the brass plate. 6BA brass studding soldered to the metal-to-glass seals carried brass flanges which supported the grids, and a flanged glass cylinder supported the anode and guard plates. Where it was necessary to give support and rigidity without making electrical connection, the brass studding was sheathed with glass tube.

The grids were constructed from 40 swg nickel wire and the anode and guard plates were molybdenum sheets sprung into place on the interior surface

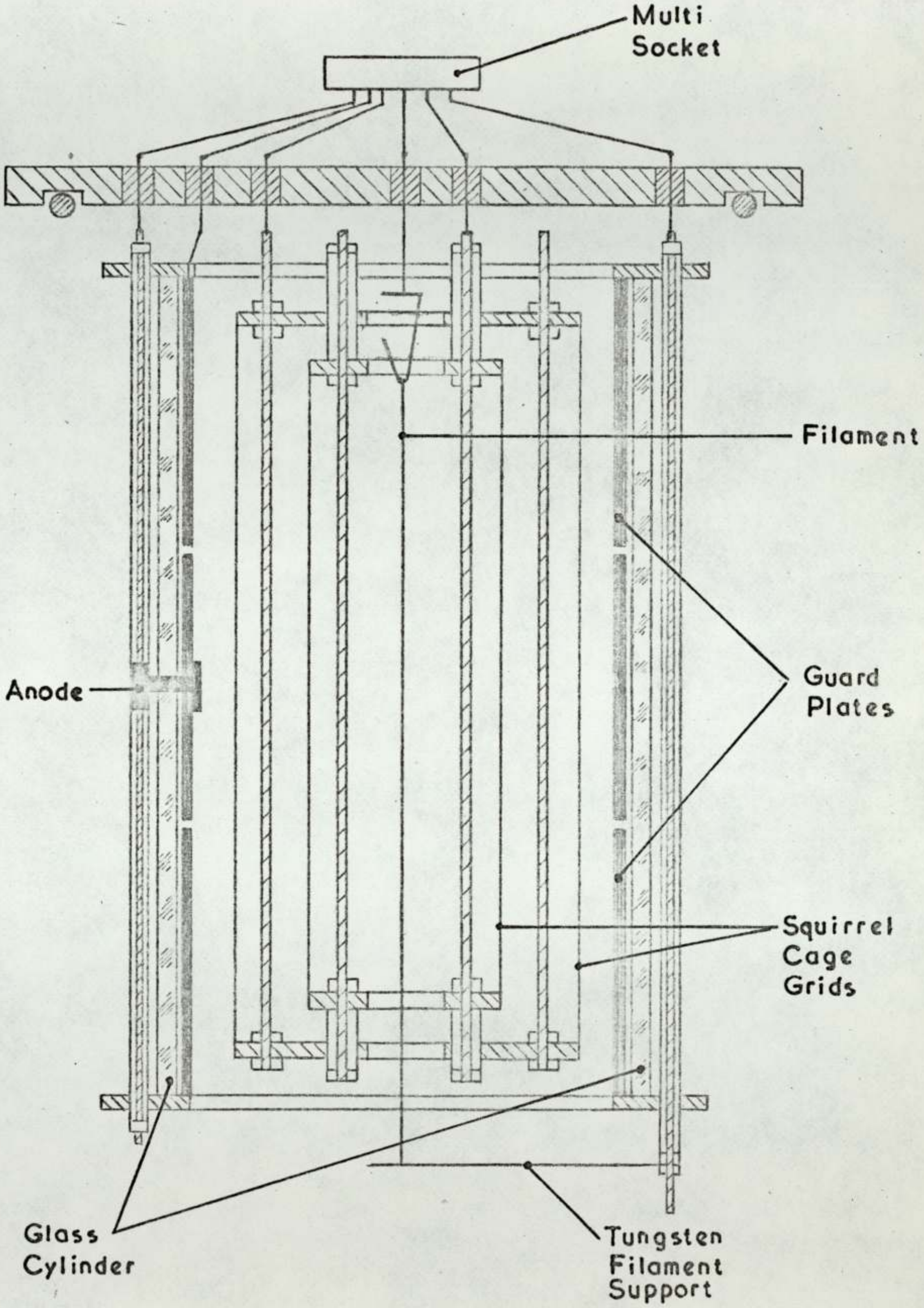


FIGURE 2

The Magnetron Assembly

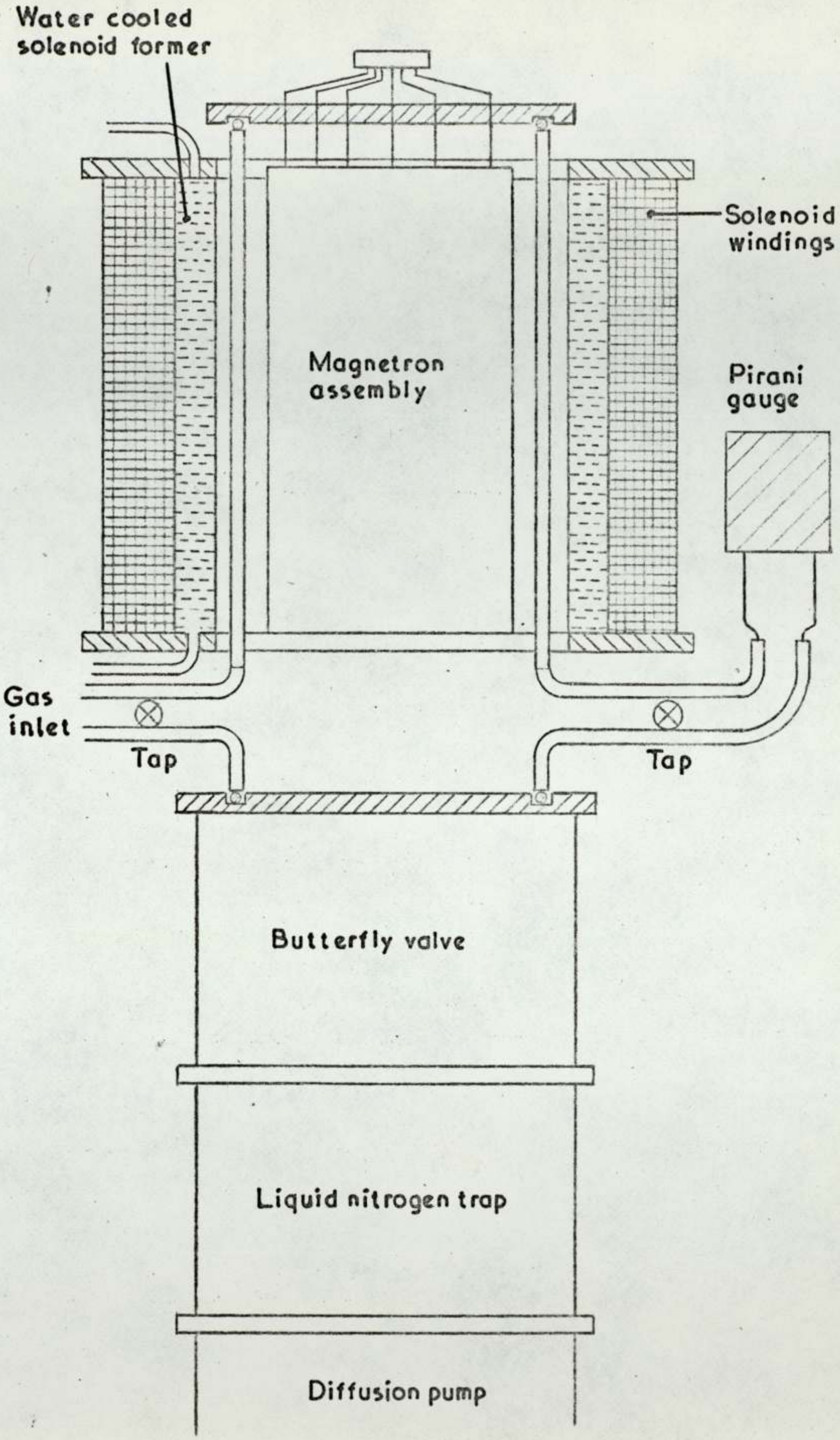


FIGURE 3

Magnetron assembly mounted in vacuum chamber and surrounded by water-cooled solenoid of the flanged glass cylinder. The guard plates were connected to the brass flanges and hence to the external circuit via the brass studding. The anode was connected by a bolt, passed through a hole in the glass cylinder, soldered to another piece of brass studding giving separate electrical connection to the external circuit.

The use of guard plates at the same potential as the anode ensured that the electron and ion currents were only collected from the central portion of the filament where the temperature is constant and where the electrostatic field is most symmetrical. The filament was a fine Pt, Ir, or W wire tensioned by a piece of 0.01 in. diam. tungsten wire.

A solenoid was constructed by winding about 2000 turns of 20 swg enamelled copper wire onto a brass water-cooled former of diameter just sufficient to pass over the pipeline magnetron bottle and so surround the magnetron assembly. The solenoid was operated at about 4 amps which produced a field sufficient to cut back the electron current 10^4 times.

The apparatus was evacuated by means of a Genevac rotary pump connected to a Genevac diffusion pump with liquid nitrogen trap and butterfly valve onto which the magnetron bottle was directly mounted. This allowed pressures of at least 10^{-5} mm Hg to be achieved.

Sample introduction was made through a side arm on the magnetron bottle via an Edwards needle valve.

The pressure was monitored using an Edwards Pirani Guage fitted to another side arm on the magnetron bottle.

The external circuitry was constructed as in Figure 4. The anode current was measured using an AVO d.c. amplifier in the 10^{-13} to 10^{-6} amps range and by a Pye Scalamp galvanometer in the 10^{-6} to 10^{-3} amps range. The d.c. potentials were applied to the filament, grids, anode and guard plates from a 120 volt dry battery. The solenoid current was drawn from a continuously-charged 120 volt bank of lead-acid accumulators.

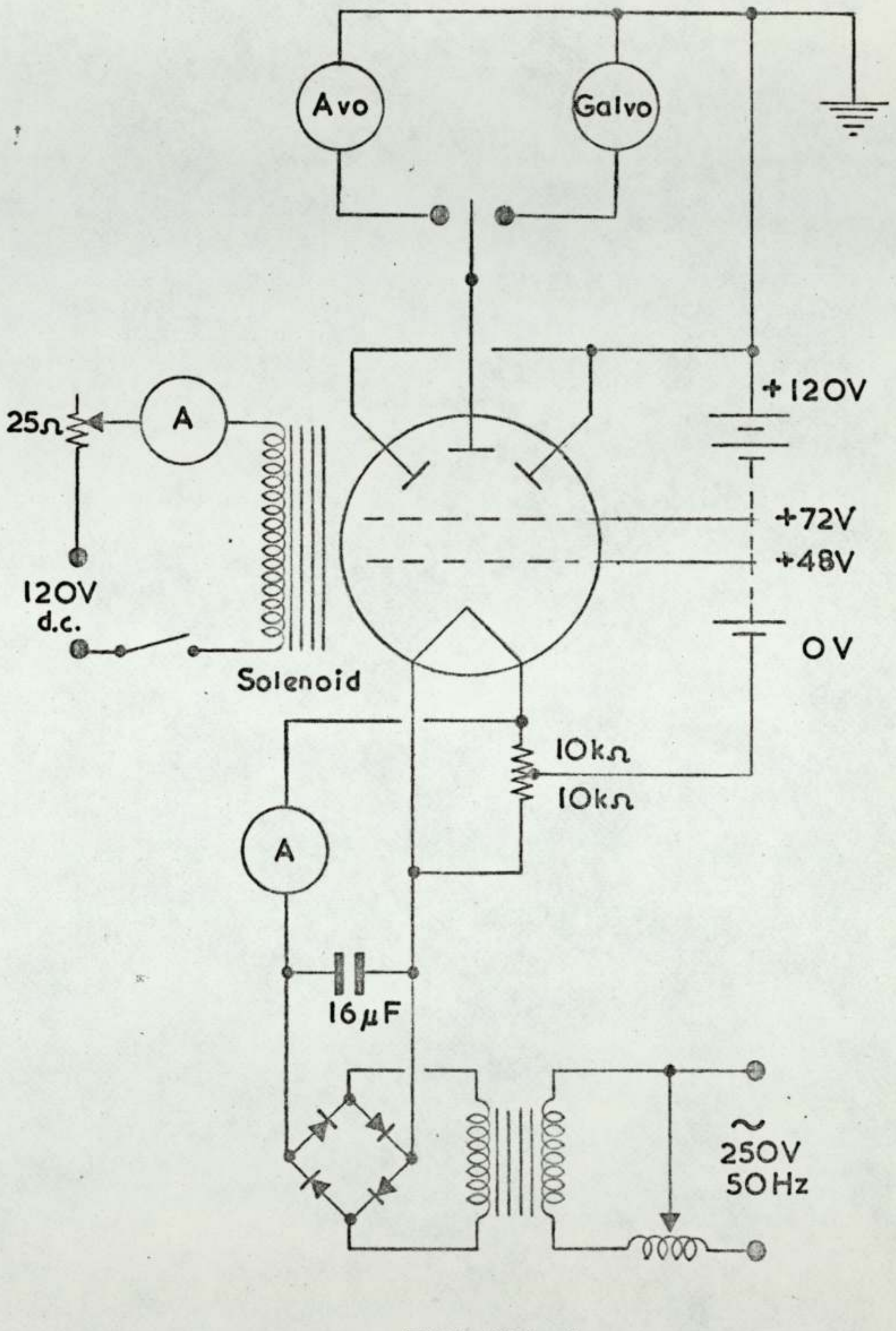


FIGURE 4

The circuit diagram

3.3 Temperature measurement.

A Leeds and Northrup disappearing-filament pyrometer was used to determine the magnetron filament temperature. Corrections to the primary pyrometer temperature have to be made to allow for the filament emissivity and the absorption by the glass walls through which the filament is observed. Accuracy of temperature determination is of prime importance for the correct evaluation of electron affinities. The emissivities of Pt, Ir, and W were taken to be 0.3, 0.3, and 0.45 respectively(42). Using a nomogram as in Figure 5, the pyrometer temperature was converted to the emissivity-corrected temperature. The glass absorption correction used was 24°K(41). Plots of filament current versus temperature squared were linear as expected from Stefan's law.

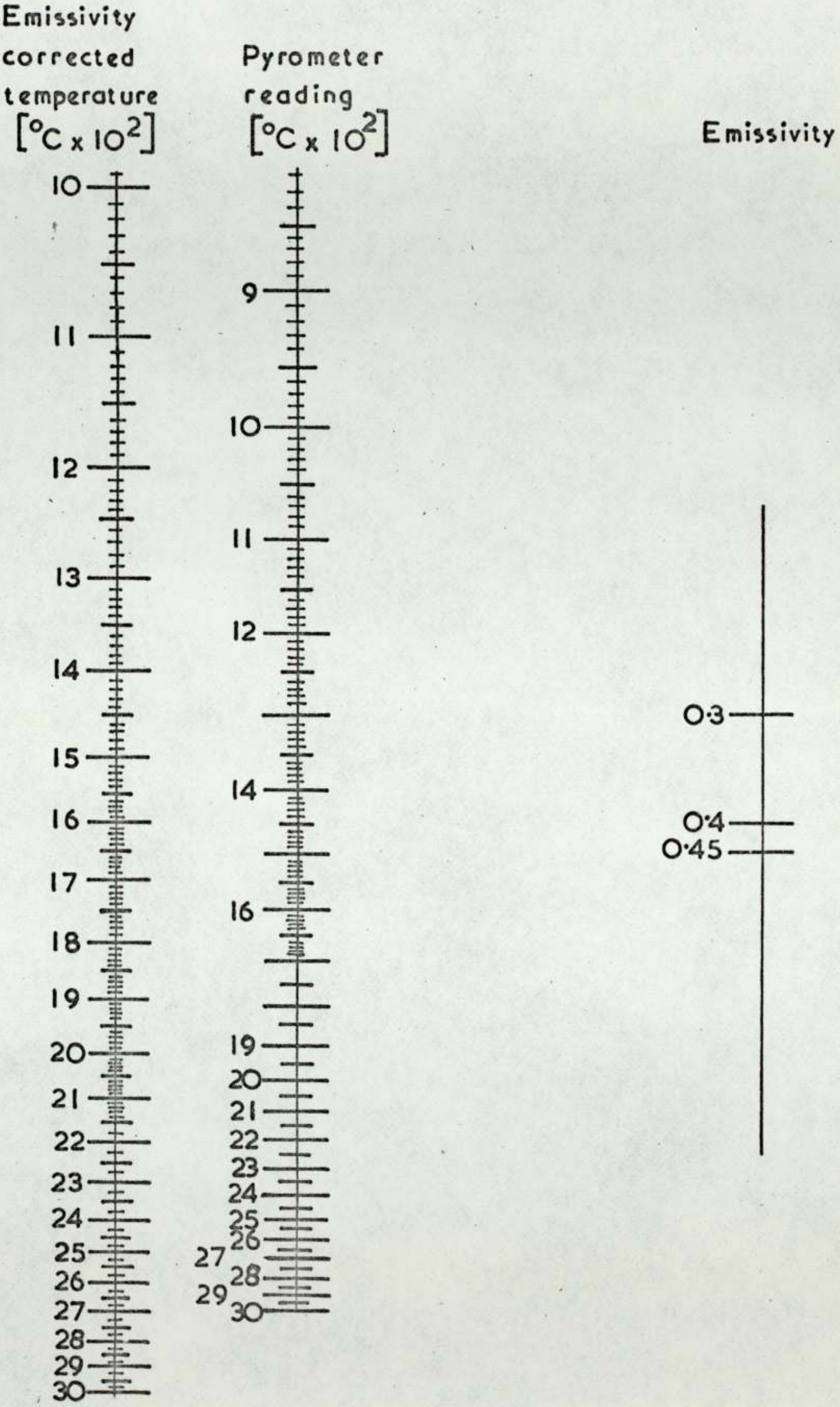


FIGURE 5

Temperature correction nomogram

3.4 The operation of the apparatus.

The thoroughly-cleaned magnetron apparatus was pumped out until the normal minimum pressure reading on the Pirani guage was obtained. This corresponded to a pressure of 10^{-5} mm Hg or less. During this stage the filament was maintained at as high a temperature as practicable to desorb any foreign material from its surface and to outgas it. As a further check on the outgassing of the apparatus, the ratio of electron and ion current to the ion current alone was measured at maximum filament temperature. When fully outgassed a value of at least 10^4 was obtained. The thermionic work function of the filament surface was then determined by measuring the electron currents over a range of filament temperatures. Richardson's equation shows that in the absence of adsorbed gas:

$$i_e = ke^{(-\chi/RT)}$$

where i_e is the electron current, k a constant, and χ is the work function. A plot of log i_e versus $\frac{1}{T}$ gives a linear plot of slope $\frac{-\chi}{R}$. The value of χ obtained was compared with the accepted value and if in good agreement this indicated that the filament surface was in a suitable condition.

The substrate was then allowed to enter the apparatus via the needle valve to maintain a pressure of about 1×10^{-3} mm Hg. The anode current was measured over a range of filament temperatures with the solenoid on to give the ion current alone, and with the solenoid off to give the ion plus electron current.

4 THEORETICAL CONSIDERATIONS RELATING TO THE EMISSION OF ELECTRONS AND NEGATIVE IONS

4.1 Theoretical treatment of ion and electron currents.

Meyer(35) postulated that an equilibrium exists at the filament surface between atoms, ions and electrons. By statistical treatment the equilibrium constant and energy change for the reaction

$$X_g + e_g \rightarrow X_g^-$$

could be determined. This gave satisfactory results for the electron affinities of the halogens(35), but was unsatisfactory for other substrates. No account however is taken in this approach of the effect on the filament of adsorption of a fragment of the substrate. Page (37) noticed that the total ion current was inversely proportional to the gas pressure. This is in direct opposition to Meyer's theory which suggests that the total current should be independent of pressure. Page interpreted this behaviour in terms of an adsorption process which resulted in a rise in the work function of the surface. When adsorption effects are taken into account the magnetron method can be successfully applied to the evaluation of the electron affinities of a wide range of substrates.

The observed energy change, or apparent electron affinity, can be represented as the energy difference between an electron in the metal filament plus a gaseous neutral species, and a gaseous negative ion with, in some cases, a fragment of the neutral species adsorbed on the filament surface or free in the gas phase. The mechanism by which transition between these initial and final states occurs involves chemisorption, ion formation on the surface, desorption of the ion and in some cases desorption of uncharged fragments. The energy diagram, Figure 6, shows that the overall energy change is:

$$W = \chi + D - E_A - Q_B \qquad (6)$$

where χ is the work function of the filament surface, D is the dissociation energy of a molecule A-B, E_A is the electron affinity of fragment A, and Q_B is the heat of adsorption of fragment B. W is the overall energy of ion formation and, since the ion current is usually compared with the electron current, the observed energy E' will be equal to $\chi - W$,

$$\text{viz: } E' = \chi - W$$

$$= E_A + Q_B - D \qquad (7)$$

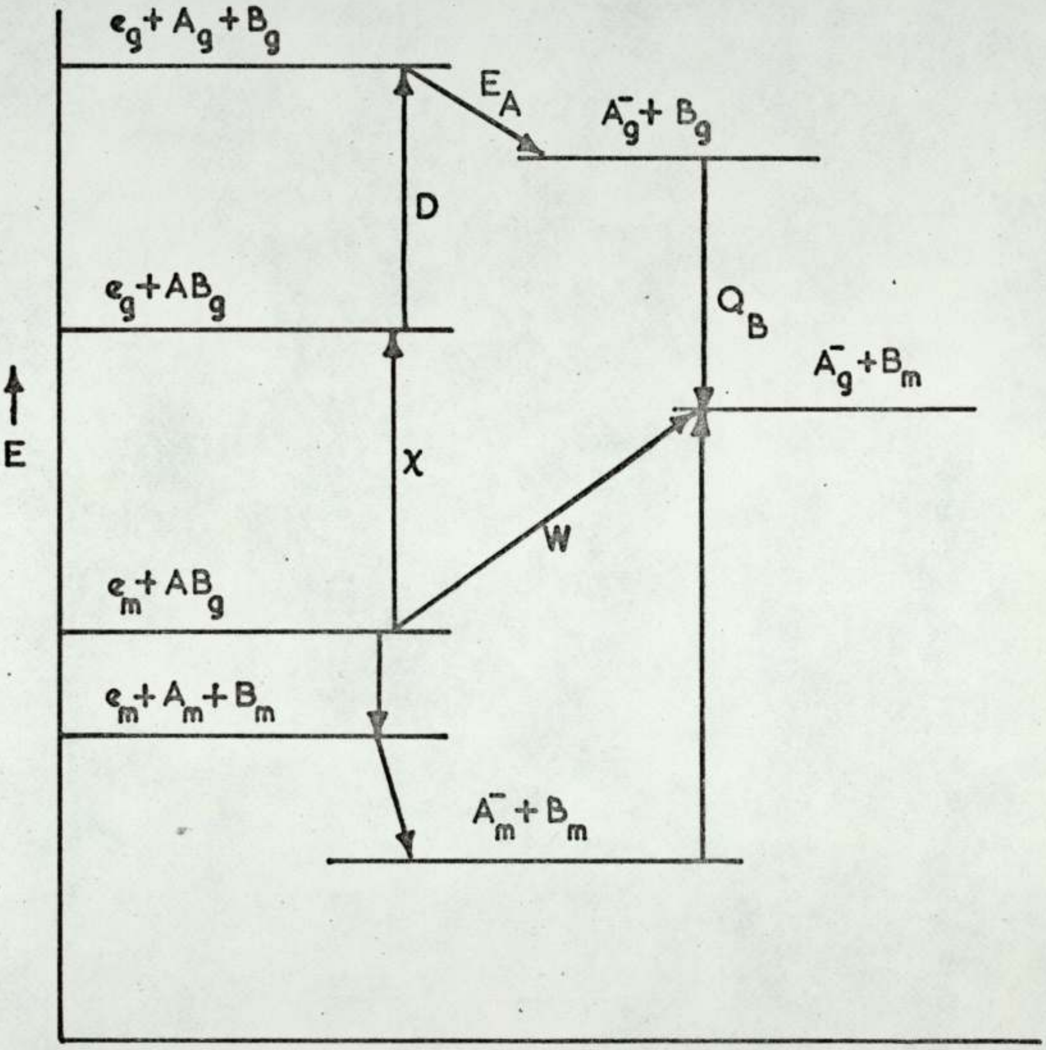


FIGURE 6

A simple kinetic treatment can be based on the above mechanism by combination with Richardson's and Langmuir's equations giving

$$\frac{i_e}{i_i} P = \frac{BT^2 k}{C k_1} e^{-\frac{(E + Q_B - D)}{RT}} \qquad (8)$$

where B, k, k_1 and C are constants, i_e and i_i are the electron and ion currents respectively, E is the electron affinity of the desorbed fragment, R is the gas constant, and T is temperature ^oK. When log $(\frac{i_e}{i_i})P$ is plotted against $\frac{1}{T}$ a linear plot is obtained of slope $\frac{E'_T}{RT}$, the apparent electron affinity at a mean temperature T divided by RT. Hence E_T, the electron affinity at a mean temperature T, can be obtained since

$$E'_T = E_T + Q - D \qquad (9)$$

Farragher(38), in an alternative approach, applied the theory of rate processes as developed by Glasstone, Laidler, and Eyring(43) to the emission of electrons and ions. It was realized that the processes of ion and electron emission were separate rate processes each characterized by its own temperature coefficient. Richardson's equation for thermionic emission derived on this basis becomes(38)

$$i_e = \frac{\bar{d}4\pi m_e(kT)^2 e}{h^3} e^{-\chi/RT} \qquad (10)$$

and the ion emission can be represented as (38)

$$i_i = \frac{\bar{d}pe}{h} \frac{Q_a^* Q_B^*}{Q_d^* Q_g} e^{-(\chi-E)/RT} \qquad (11)$$

where Q_a^* is the reduced partition function for adsorption, Q_g the partition function for unit volume, Q_B^* the partition function of B in its transition state, Q_d^* the partition function relating to desorption, and $\bar{d}$ is a transmission coefficient

Separating the translational partition function from the internal partition function, and assuming that the latter is identical for the gas phase molecule and for the transition states for adsorption and desorption:

$$\frac{Q_a^*}{Q_g} = \frac{h}{(2\pi MkT_g)^{\frac{1}{2}}} \qquad (12)$$

$$\frac{Q_B^*}{Q_d^*} = \frac{Q_i}{Q_m} \qquad (13)$$

where Q_i and Q_m are the internal partition functions of the transition state ion and gas phase molecule respectively

gives

$$i_i = \frac{\bar{d}pe}{(2\pi MkT_g)^{\frac{1}{2}}} \frac{Q_i}{Q_m} e^{-(\chi-E)/RT} \qquad (14)$$

and the ratio of the electron and ion currents from eqns. (14) and (10) is

$$\frac{i_e}{i_i} = \frac{4\pi M_e (\mathbf{k}T)^2 (2\pi M\mathbf{k}T_g)^{\frac{1}{2}}}{h^3 p} \frac{Q_m}{Q_i} e^{(-E/RT)} \qquad (15)$$

The ratio Q_m/Q_i is of importance because it has some temperature dependence which must be allowed for when E_T is corrected to standard conditions. An accurate correction for this temperature dependence demands an accurate evaluation of Q_m/Q_i. However, this requires a knowledge of band frequencies in the transition state which can only be crudely estimated. Furthermore, since vibrational energy transfer is a slow process, the actual vibrational temperature may be between the gas temperature and the filament temperature, thus rendering an accurate temperature correction impossible. In practice the classical approach is resorted to, whereby a temperature dependence of ½ RT is ascribed to each rotational, vibrational and translational degree of freedom lost in the ion formation reaction. The temperature correction applied depends on the type of ion formation reaction.

N.B. The classical dependence of RT per degree of vibrational freedom has not been used because it is assumed that as vibrational excitation is normally slower than translational and rotational excitation it does not contribute fully.

4.2 Types of ion formation reaction and their temperature correction.

Type 1, Direct capture

$$AB + e \rightarrow AB^-$$

No dissociation occurs, so the internal partition function for the ion and the molecule can be assumed to be similar except for the electronic contribution(38). The ground state molecule will probably be a singlet and the ion a doublet.

Hence $\frac{Q_m}{Q_i} = \frac{1}{2}$

viz: $\frac{i_e}{i_i} = \frac{AT^2}{2} e^{-E'_T/RT}$

so that

$$\frac{d\left(\log \frac{i_e}{i_i}\right)}{d\,\frac{1}{T}} = -\frac{E'_T}{R} + 2RT$$

In this case $E_T = E'_T$ since no dissociation or adsorption occurs and $E_T = E + 2RT$. (16)

Or classically since three translational degrees of freedom are lost:

$$E_T = E + \frac{3}{2} RT \qquad (17)$$

Type 2, Weak bond fission.

The breaking of a bond of less than about 70k cal. mole^{-1} does not contribute to the heat of reaction at the filament and this is ascribed to a pre-equilibrium whereby the substance behaves as if it were composed of the free radical. The ion formation process is equivalent in energy to the direct capture process and therefore involves the same temperature correction.

Type 3, Strong bond dissociation without adsorption.

In this case bond dissociation occurs during ion formation. The internal partition functions for the molecule and the ion cannot be assumed to be similar. If the transition state frequency of the bond which breaks is assumed to be 100 cm^{-1} and the frequency of vibration in the normal molecule is 1000 cm^{-1} then it can be shown(38) that

$$E_T' = E' + 2RT \qquad (18)$$

The classical approach for the reaction

$$AB_g + e_g \rightarrow A_g^- + B_g$$

where B is a monatomic species and where A is a polyatomic species shows that three vibrational degrees of freedom are lost so that

$$E_T' = E' + \frac{3}{2} RT \qquad (19)$$

(see footnote page 31)

Type 4, Dissociation with adsorption.

If the molecule AX is attached to the surface by the atom X which is to be adsorbed, and it is assumed that the rate-determining step is the stretching of the A-X bond where A is the electron acceptor, then considering the other two vibrations of the A-X bond and the surface to X bond gives(38)

$$E_T' = E' + 3RT \qquad (20)$$

by evaluation of Q_m/Q_i using the frequency assumptions as before.

Classically if A is polyatomic, three vibrational, two rotational and one translational degrees of freedom are lost so that, again,

$$E_T' = E' + 3RT \qquad (20)$$

(see footnote page 31)

The apparent electron affinity was found experimentally at T^oK. In this dissertation equations (16) (18) and (20) have been used to correct the results to 0^oK to be consistent with other published data$^{(5)}$.

4.3 The entropy of reaction$^{(38)(36)}$.

Combination of equations (10) and (11) with the substitution of Q^* for

$$\frac{2(2\pi m_e kT)}{h^2}$$

gives

$$\frac{i_e}{i_i} = \frac{KT}{p} \frac{Q_d^* \, Q_g \, Q^*}{Q_a^* Q_B^* \cancel{Q^*}} e^{\left[E_a/RT_g\right]} e^{\left[-(E/RT)\right]} \qquad (21)$$

which can be written in the form:

$$\frac{i_e}{i_i} = \frac{kT}{p} K_1 K_2 \qquad (22)$$

where K_1 and K_2 are the concentration equilibrium constants for the reactions

$$AB_{(a)}^{*} \rightleftharpoons AB_{(g)}$$

$$AB^{*-} \rightleftharpoons AB^{*}_{(d)} + e^{*}$$

If ΔG_1 and ΔG_2 are the associated Gibb's free energy changes, then (22) becomes:

$$\frac{i_e}{i_i} = \frac{kT}{p}\, e^{(-\Delta G_1/RT_g)}\, e^{(-\Delta G_2/RT)} \qquad (23)$$

$\Delta G = \Delta H - T\Delta S$ therefore:

$$\frac{i_e}{i_i} = \frac{kT}{p}\, e^{-\Delta H_1/RT_g} . e^{+\Delta S_1/R} . e^{-\Delta H_2/RT} . e^{\Delta S_2/R} \qquad (24)$$

If the adsorption process is non-activated, $\Delta H = 0$, and defining $\Delta S = \Delta S_1 + \Delta S_2$ then

$$\frac{i_e}{i_i} = \frac{kT}{p}\, e^{(-\Delta H_2/RT)} . e^{(\Delta S/R)} \qquad (25)$$

Taking logs and differentiating with respect to T and noting that

$$\frac{d(\log \frac{i_e}{i_i})}{dT} = E'_T/RT^2 \text{ gives}$$

$$E'_T = RT + \Delta H_2 \qquad (26)$$

Hence taking logs of (25), re-arranging and substituting for ΔH_2 gives:

$$\Delta S = R(\log \frac{i_e}{i_i} - \log \frac{kT}{p}) + \frac{E'_T}{T} - R \qquad (27)$$

Inserting numerical values for the constants, then

$$\Delta S = 4.56(18.98 + \log \frac{i_e}{i_i} - \log \frac{T}{\rho}) + \frac{E'_T}{T} - 1.98 \qquad (28)$$

T is in ^oK, R ~~and E'_T are~~ is in cal.mole^{-1} $^oK^{-1}$, ρ is in mm Hg, ΔS is the entropy change in entropy units, E'_T in cal.mole^{-1}.

Farragher$^{(38)}$ found that the value of the entropy change was characteristic of the mode of ion formation and could, therefore, be used to determine the reaction type, as follows:

ΔS of 110 ± 17 e.u. - types 1 & 2 processes

ΔS of 53 ± 7 e.u. - type 3 process

ΔS of 82 ± 5 e.u. - type 4 process

Such a diagnostic test is of considerable utility since the type of reaction and the nature of the negative ion formed can only be deduced indirectly by considerations of energy.

5. MEASUREMENT OF THE ELECTRON AFFINITY OF SOME SULPHUR COMPOUNDS

Sulphur hexafluoride is an electronegative gaseous insulator of commercial importance, much used in high current high voltage switchgear in which it acts as an insulator with excellent arc quenching properties. The electron affinity of sulphur hexafluoride has been measured by Page who obtained a value of 35k cal.mole^{-1} by the magnetron method. Values of 83.5 and 82.8k cal.mole^{-1} were obtained by Kay and Page(46) for sulphur pentafluoride radical in the magnetron. These values indicate an exceptionally high stability for the sulphur pentafluoride negative ion and reasonably allow explanation of the arc quenching ability of sulphur hexafluoride in terms of removal of electrons from the arc plasma. The stabilities in the magnetron of the negative ions formed from sulphur tetrafluoride, sulphuryl fluoride and carbon disulphide were measured to provide a better understanding of the electron affinity of sulphur compounds. Comparison of these values with those obtained for perfluorocarbons is of interest.

5.1 Sulphur tetrafluoride.

Sulphur tetrafluoride supplied in a lecture bottle by Cambrian Chemicals Limited was passed directly into the magnetron apparatus so as to maintain a pressure of 1×10^{-3} mm Hg. Platinum filaments were used and ion and electron currents were measured over a filament temperature range of 1500° to 1800°K. A plot of the logarithm of the ratio of these currents versus reciprocal temperature showed two distinct, approximately linear regions. These corresponded to the temperature ranges 1500° to 1650°K and 1650° to 1750°K. A typical plot is given in Figure 7.

5.1.1 The 1500° to 1650°K region.

The slope of log i_e/i_i versus $1/T$ gave a mean apparent electron affinity of -11.5 ± 3.4k cal.mole^{-1}. The entropy of reaction calculated from equation (28) was 60.7 e.u. This is indicative of a type 3 process of dissociative capture without adsorption. The following process was therefore postulated:

$$SF_4 + e \rightarrow SF_3^- + F$$

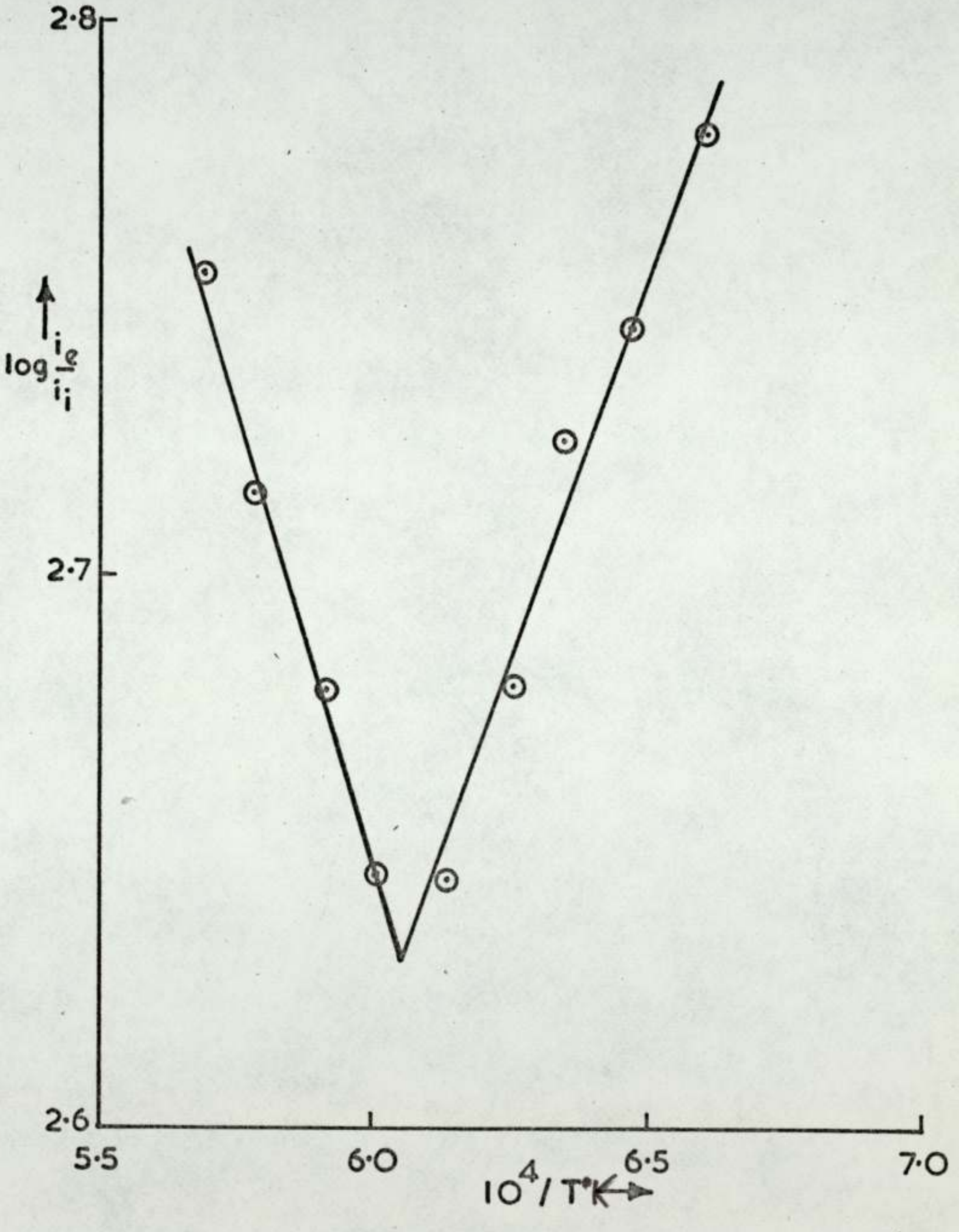


FIGURE 7

Ion-electron current ratios for SF_4

The temperature correction for the apparent electron affinity from equation (18) is 2RT. The apparent electron affinity at 0°K then becomes -17.6 ± 3.4k cal.mole^{-1}.

$$E' = E_{SF_3} - D$$

Taking the $SF_3 - F$ bond energy to be 80k cal.mole^{-1}(52) then:

$$E_{SF_3} = -17.6(\pm 3.4) + 80\text{k cal.mole}^{-1}$$

Hence

$$E_{SF_3} = 62.4 \pm 3.4\text{k cal.mole}^{-1}.$$

Other experimental determinations of the electron affinity of SF_3 do not appear to have been made. However this value appears reasonable if compared with the values 83.5 and 82.8k cal.mole^{-1} obtained by Kay & Page(46) for SF_5.

5.1.2 The 1650° to 1750°K region.

An apparent electron affinity of $+ 14.7 \pm 5.3$k cal.mole^{-1} was obtained from the slope of log i_e/i_i plotted against 1/T.

The entropy of reaction from equation (28) was 77.4 e.u. This value is indicative of a type 4 process of dissociative capture with adsorption. However, the apparent electron affinity is incompatible in energy with such a process or with any other simple process. It is probable therefore that more complex reaction behaviour occurs in this temperature region.

5.2 Sulphuryl fluoride.

Sulphuryl fluoride was supplied in a lecture bottle by Cambrian Chemicals Limited. This was passed into the magnetron apparatus where the pressure was maintained at 1 X 10^{-3}mm Hg. Platinum filaments were used and ion and electron currents were measured over a 1500° to 1800°K temperature range. Plots of the logarithm of the ratio of these currents versus reciprocal temperature showed two distinct regions corresponding to the temperature ranges 1550° to 1650°K and 1650° to 1750°K. Figure 8 shows a typical plot.

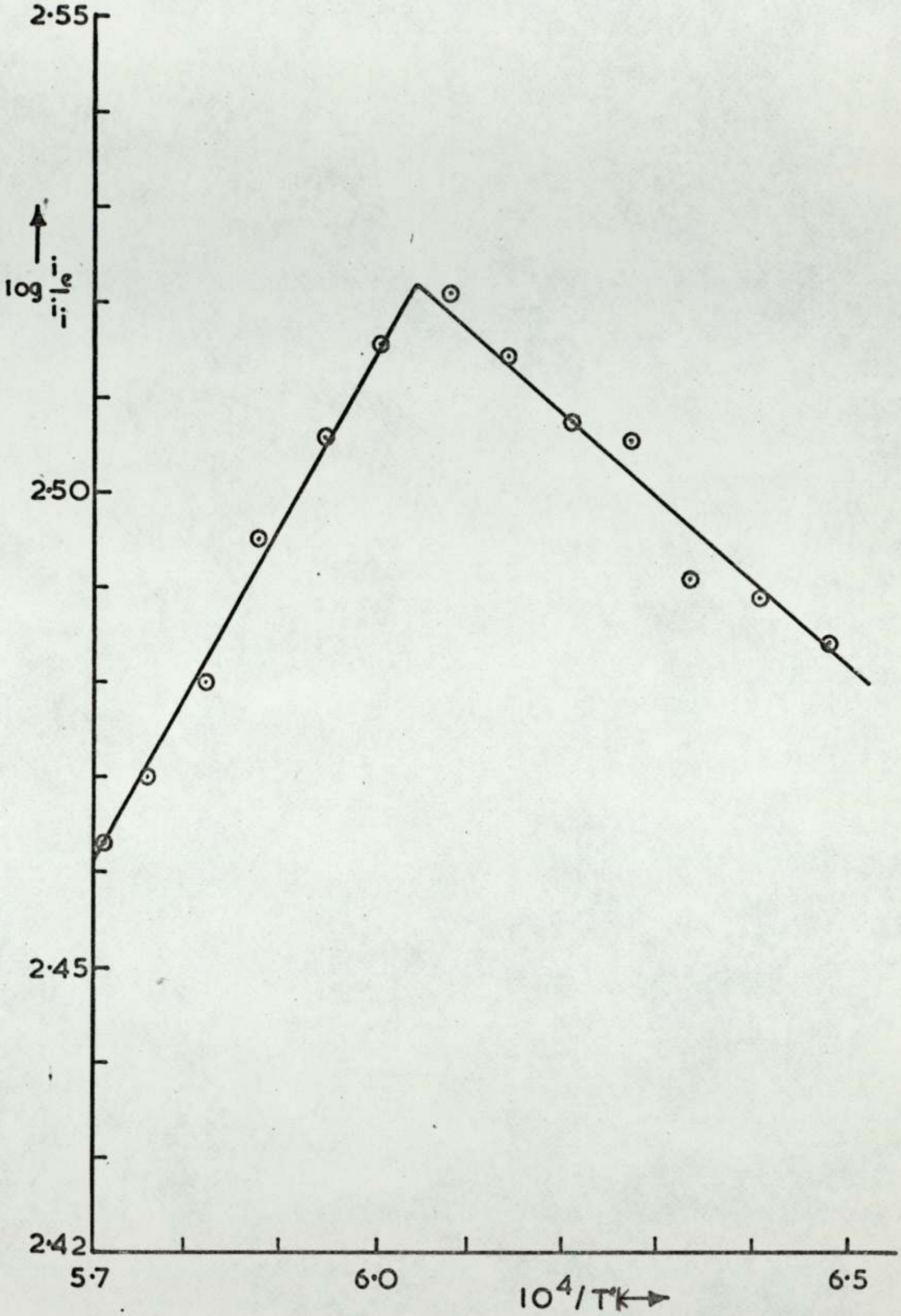


FIGURE 8

Ion-electron current ratios for SO_2F_2

5.2.1 The 1550° to 1650°K region.

In this temperature region a slope corresponding to an apparent electron affinity of + 9.0 ± 2.1k cal.mole^{-1} was observed. The entropy of reaction from equation (29) was calculated to be 74.9 e.u. This is intermediate between the values typical of type 3 and type 4 processes. The apparent electron affinity appears to be incompatible with any single simple process and therefore it is probable that two or more processes are occurring simultaneously.

5.2.2 The 1650° to 1750°K region.

The slope of the plot in this temperature region corresponded to an apparent electron affinity of -9.4 ± 3.5k cal.mole^{-1}. A typical plot is given in Figure 8. From equation (28) the entropy of reaction was calculated to be 64.0 e.u. indicating the possibility of a type 3 process of dissociative capture without adsorption. A probable process in concord with this result was postulated as follows:

$$SO_2F_2 + e \rightarrow SO_2F^- + F$$

A correction of the apparent electron affinity to standard conditions by means of equation (18) gave a value of -16.2 ± 3.5kcal.mole^{-1}. Since:

$$E' = E - D$$

then taking a value of 80k cal.mole^{-1} for the O_2FS-F bond energy gives:

$$E = 63.8 \pm 3.5\text{k cal.mole}^{-1}.$$

Other experimental values for the electron affinity of SO_2F are not available for comparison. The value is very similar to that observed with SF_3 and does not appear unreasonable when compared with that of SF_5.

5.3 Carbon disulphide.

Carbon disulphide supplied by Hopkin & Williams was placed in a small flask connected via a side arm and needle valve to the magnetron bottle. Evaporation into the magnetron was adjusted until a pressure of 1×10^{-3}mm Hg was maintained. Platinum and tungsten were used as filament materials. However, both of these types of filament had only a limited useful lifetime. After approximately half an hour in the presence of the carbon disulphide, ion and electron currents would cease to behave reversibly with filament temperature. This behaviour was preceded by an increase in the work function of the filament surface. It is probable that scission of the carbon disulphide molecules at the heated filament produces fragments, probably sulphur atoms, which are very strongly adsorbed. Eventually these may cover nearly all of the available adsorption sites. Tungsten filaments could be made to give a longer useful life than could platinum, probably because prolonged heating at higher temperatures allowed some desorption to occur. Ion and electron currents using tungsten filaments in the range 1650° - 2000°K gave an approximately linear reproducible log i_i/i_e versus I/T relation, whereas results using platinum filaments were not sufficiently reproducible to be usable.

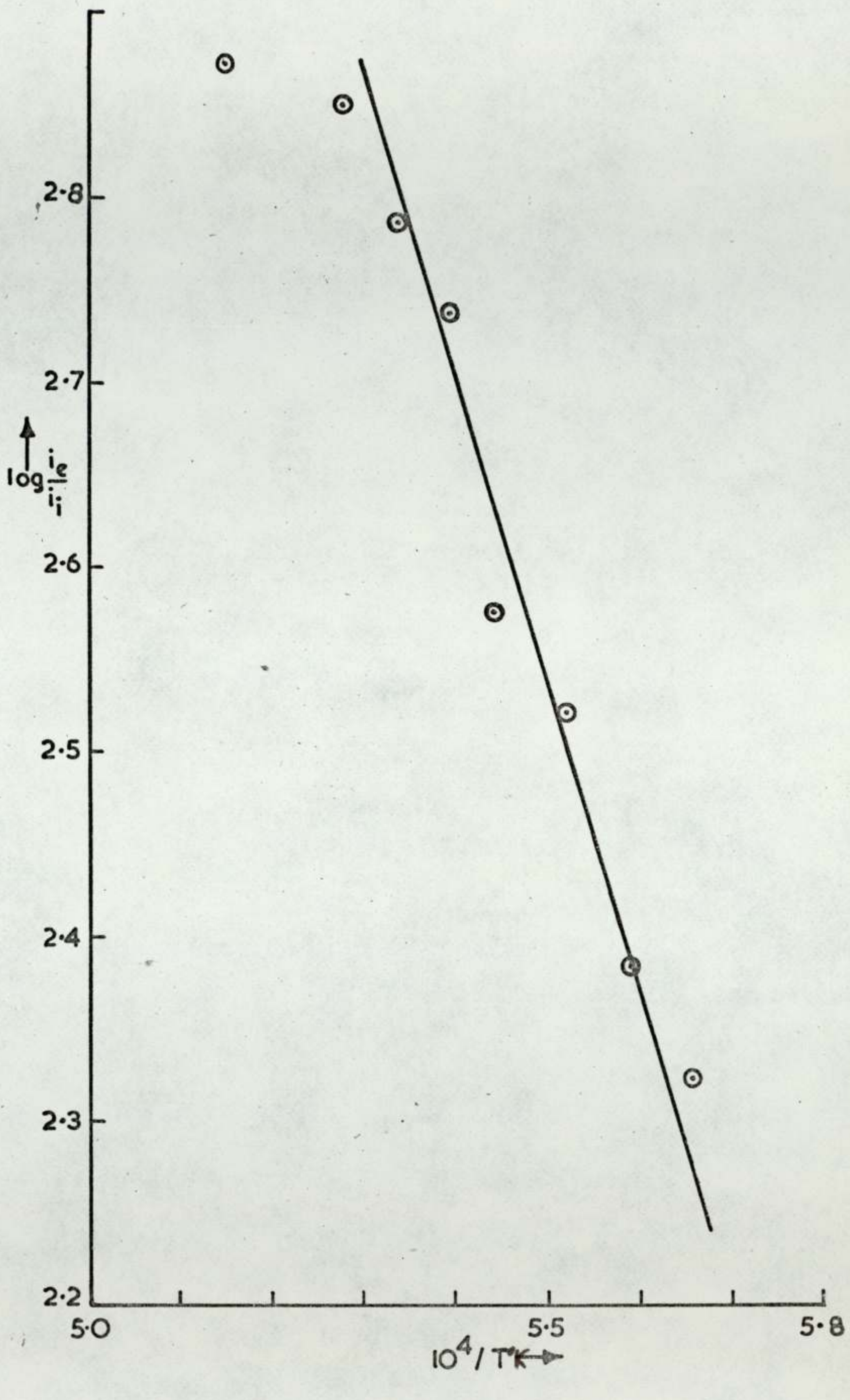


FIGURE 9

Ion-electron current ratios for CS_2

A typical plot is given in Figure 9. The slope of these plots corresponded to a mean apparent electron affinity of 68 ± 3.2k cal.mole^{-1}.

The entropy of reaction calculated from equation (29) was 105 e.u. indicative of a type 1 direct capture process. Allowing for the mean elevation of work function of the tungsten surface which was 28k cal.mole^{-1} the apparent electron affinity becomes 40 ± 3.2k cal.mole^{-1}. Correcting this value according to equation (16) i.e. by 2RT gives a value of 33.1 ± 3.2k cal.mole^{-1} for the apparent electron affinity under standard conditions. It is postulated that the following processes occur in parallel:

$$CS_2 + e \rightarrow CS_2^-$$

$$CS_2 \rightarrow CS + S_{ads.}$$

The CS fragment in the latter process may also be adsorbed. If the first process is assumed to be the only contributor to the formation of negative ions, then the electron affinity of carbon disulphide is 33.1 ± 3.2k cal.mole^{-1}.

The stability of this ion will be due to the interaction of the negative charge with the polarizable CS group.

The energy of this electro-static interaction is readily amenable to calculation. If the polarizability of the CS group is α_{CS} and the distance between the negative charge and the centroid of the polarization elipsoid, taken as the centre of the CS bond, is r, then the energy of electrostatic interaction is given by(53):

$$W = -\tfrac{1}{2}\,\frac{e^2}{r^4}\;\alpha_{CS}$$

$$\text{Since } \alpha_{CS} = \tfrac{1}{2}\alpha_{CS_2}$$

$$= \frac{3}{4\pi N}\;\frac{n^2-1}{n^2+2}\;\frac{M}{D}$$

where n is the refractive index and D the density, substitution of known values gives:

$$W = -38.5\text{k cal.mole}^{-1}.$$

This predicted value of 38.5k cal.mole^{-1} for the electron affinity of carbon disulphide is in reasonable agreement with the measured value of 33.1 ± 3.2k cal.mole^{-1}. Better agreement would no doubt be obtained by refinement of the bond length estimate. The $C-S^-$ bond will be slightly longer than the C-S bond giving a lower predicted electron affinity for carbon disulphide. It is of interest that the stability of the carbon disulphide negative ion is similar to that of the sulphur hexafluoride negative ion.

6. MEASUREMENT OF THE ELECTRON AFFINITY OF SOME PERFLUOROCARBON COMPOUNDS

Burdett(39) has studied the magnetron behaviour of some fluoro-aromatic compounds and Goode(36) has studied the formation in the magnetron of CF_3^- from aliphatic fluorocarbons. The present work extends the study of fluorocarbon negative ions in the magnetron by examining the stability of those formed from perfluoropropane, perfluorocyclobutane, perfluorobutene - 2, undecafluorocyclohexane, and perfluorodecalin.

6.1 Perfluoropropane.

Perfluoropropane supplied by Cambrian Chemicals Limited was passed into the magnetron apparatus and the pressure maintained at 1 X 10^{-3} mm Hg. Platinum filaments were used. Ion and electron currents were measured over a filament temperature range of 1450° to 1800°K. Plots of the logarithm of the ratio of these currents versus reciprocal temperature showed three regions corresponding to the temperature ranges 1450° to 1550°K, 1560° to 1660°K, and 1670° to 1770°K. A typical plot is shown in Figure 10.

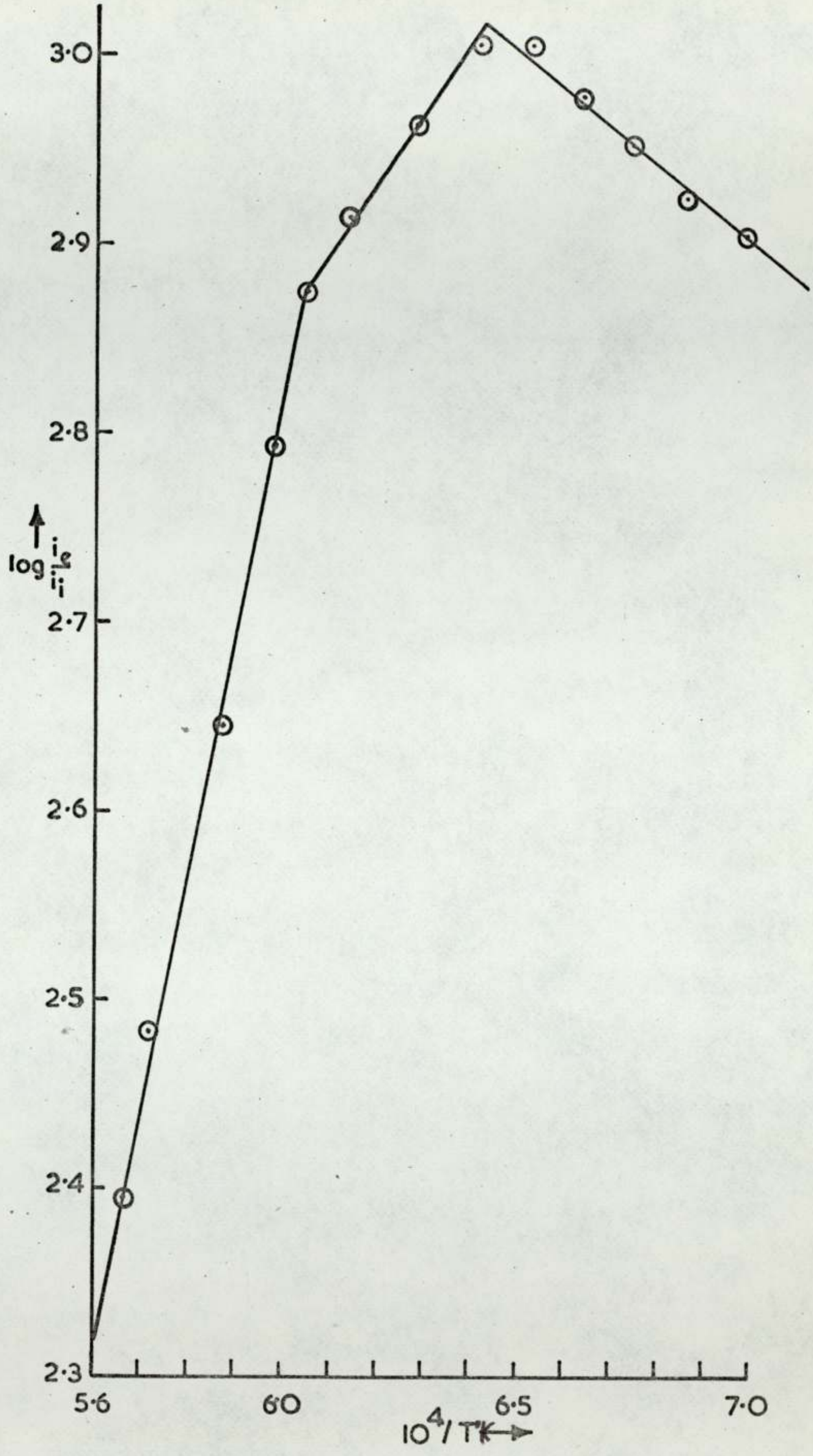


FIGURE 10

Ion-electron current ratios for C_3F_8

6.1.1 1450° to 1550°K region.

An apparent electron affinity of + 6.9 ± 1.5k cal.mole^{-1} was observed in this temperature region. The entropy of reaction calculated by means of equation (28) was 75.0 e.u. This is indicative of a dissociative capture with adsorption process. However, the apparent electron affinity value does not appear to be compatible with such a process or with any other simple process. The reaction behaviour in this region is probably complex in nature.

6.1.2 1560° to 1660°K region.

In this temperature region the apparent electron affinity was -15.1 ± 4.2k cal.mole^{-1}. The entropy change of reaction calculated from equation (28) was 60.4 e.u.

This value is indicative of a type 3 process of dissociative capture without adsorption. Consideration of reaction energy terms showsthat the only possible process is dissociative capture with adsorption. The entropy of reaction is not in this instance therefore a reliable guide.

Correction of the apparent electron affinity to $0^{\circ}K$ by means of equation (20) gives a value of -24.5 ± 4.2k cal.mole^{-1}.

Since $E' = E + Q - D$

substituting values of 51.1k cal.mole^{-1} for the heat of adsorption of fluorine on platinum(36) and 122.2k cal.mole^{-1} for the dissociation energy of the $F_7C_3 - F$ bond(47) gives

$$E = 46.6 \pm 4.2\text{k cal.mole}^{-1}.$$

$C_3F_7^-$ is formed by the process

$$C_3F_8 + e \rightarrow C_3F_7^- + F_{ads}$$

and has a stability of 46.6 ± 4.2k cal.mole^{-1}.

This value is not dissimilar to that obtained for CF_3^- in the magnetron(36). Such a similarity is in accord with that of the ions themselves.

6.1.3 1670° to 1770°K region.

An apparent electron affinity of -45.7 ± 3.4k cal.mole^{-1} was found in this temperature region. The entropy change calluated according to equation (28) was 41.0 eV. By consideration of the energies involved, neither the entropy nor the apparent electron affinity are compatible with any simple process. Complex reaction behaviour probably occurs, therefore.

6.2 Perfluorocyclobutane.

Perfluorocyclobutane supplied by Cambrian Chemicals Limited was passed into the magnetron apparatus and the pressure maintained at 1×10^{-3} mm Hg. Platinum filaments were used, and the ion and electron currents corresponding to filament temperatures in the range 1500° to 1800°K were measured. The plots of the logarithm of the ratio of these currents versus reciprocal temperature showed two distinct regions corresponding to the temperature ranges 1500° to 1650°K and 1680° to 1780°K. A typical plot is shown in Figure 11.

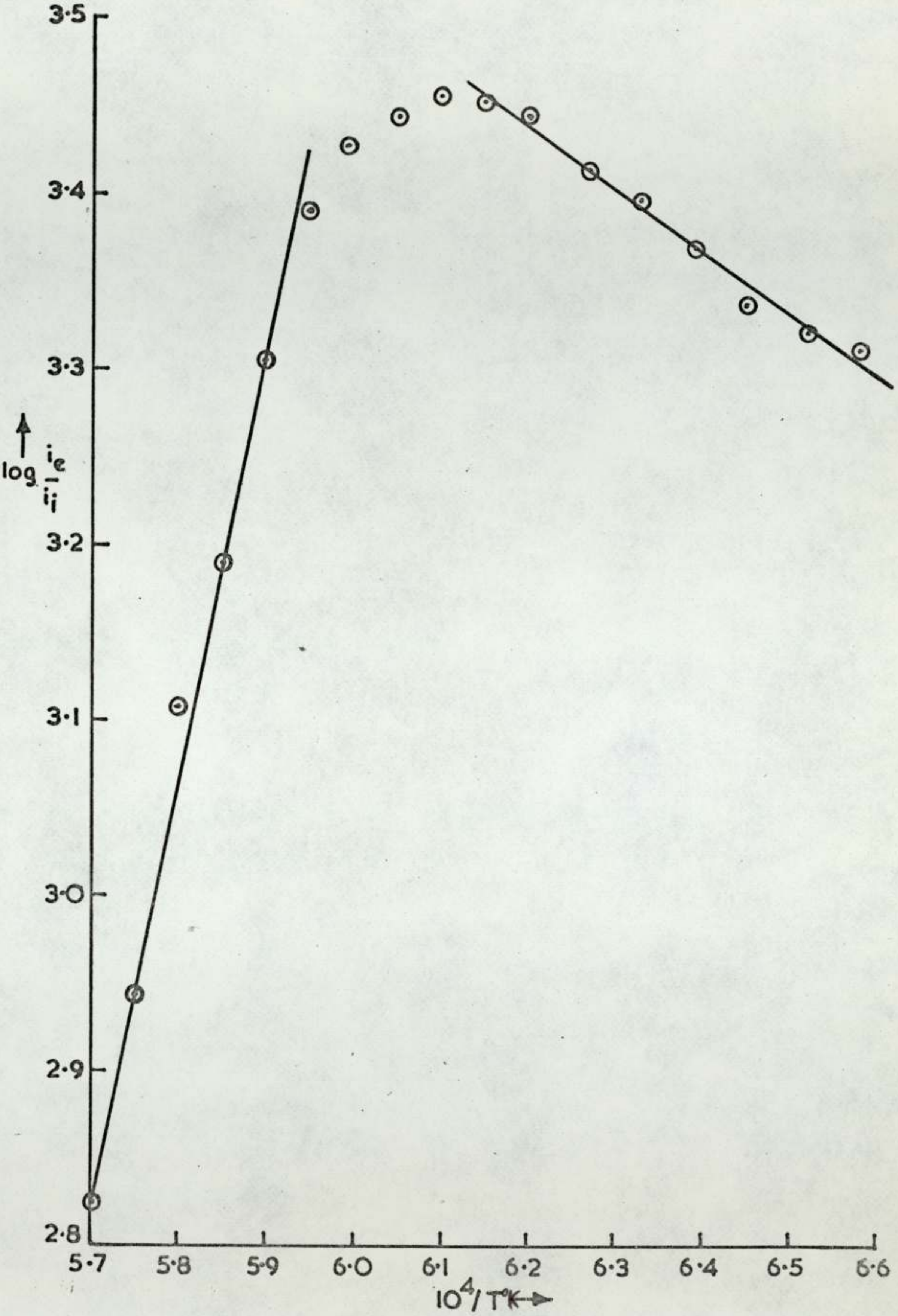


FIGURE 11

Ion-electron current ratios for c-C_4F_8

6.2.1 1500° to 1650°K region.

In this temperature region an apparent electron affinity of + 17.2 ± 3.5k cal.mole^{-1} was obtained. From equation (28) the entropy of reaction was calculated to be 83.0 e.u.

Perfluorocyclobutane is known to depolymerize at these temperatures to give two molecules of perfluoroethylene by a direct unimolecular process(48)(49). At the filament temperatures used this thermal process is very favourable and probably occurs in the magnetron. Desorption of the perfluoroethylene formed as negative ions is postulated thus:

$$c - C_4F_8 + 2e \rightarrow 2\,C_2F_4^-$$

Equilibrium studies at 550°C have allowed measurement of the heat of dimerization of perfluoroethylene. A value of - 49.8k cal. mole^{-1} was obtained(50). Hence the heat of depolymerization of perfluorocyclobutane when corrected to 0°K becomes + 93.2k cal.mole^{-1}.

A temperature correction of 3RT must be applied to the apparent electron affinity because the process envisaged involves a loss of three translational and six vibrational degrees of freedom and a gain of three rotational degrees of freedom. (see page 31) The apparent electron affinity at $0^\circ K$ is then + 7.9 ± 3.5k cal.mole^{-1}.

Since $E' = 2E - D$

where in this instance D is the heat of depolymerization, then

$$E = 50.6 \pm 3.5\text{k cal.mole}^{-1}.$$

A value of 50.6 ± 3.5 cal.mole^{-1} for the electron affinity of perfluoroethylene is higher than might be expected. However, there are few structurally similar compounds whose electron affinities have been measured to enable comparison. Tetracyanoethylene, with a more extensive π-orbital system than perfluoroethylene, has an electron affinity of 66.4k cal.mole^{-1}.

6.2.2 1680° to $1780^\circ K$ region.

The apparent electron affinity in this region was somewhat variable and averaged -212k cal.mole^{-1}. This can only be interpreted in terms of complex behaviour probably involving more extensive degradation of the perfluorocyclobutane molecules on the filament.

6.3 Perfluorobutene - 2

Perfluorobutene - 2 supplied by Cambrian Chemicals Limited was passed into the magnetron apparatus and the pressure maintained at 1 X 10^{-3} mm Hg. Platinum filaments were used. Ion and electron currents were measured for filament temperatures in the range 1500° to 1800°K. The plots of the logarithm of the ratio of these currents versus reciprocal temperature showed two distinct regions corresponding to filament temperature ranges 1500° to 1700°K and 1700° to 1800°K. A typical plot is shown in Figure 12.

6.3.1 1500° to 1700°K region.

The apparent electron affinity observed in this region was -0.6 ± 1.1k cal.mole^{-1}. The entropy change of reaction was calculated to be 72 e.u. from equation (28). Such a value is indicative of a type 4 process of dissociative capture with adsorption. The apparent electron affinity appeared to be compatible in energy with the process

$$C_4F_8\text{-}2 + e \rightarrow C_4F_7^- + F_{ads}$$

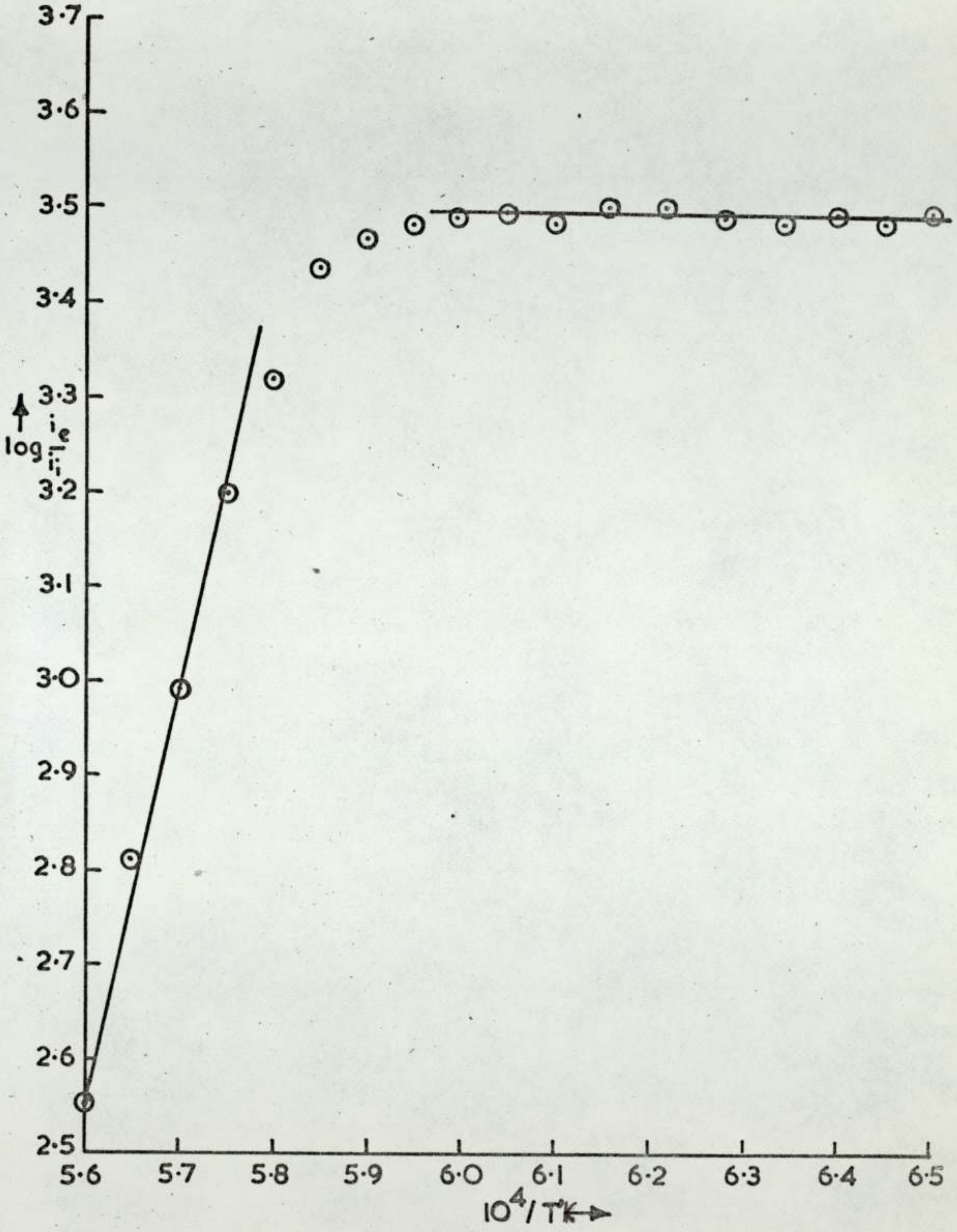


FIGURE 12

Ion-electron current ratios for C_4F_8-2

Correction of the apparent electron affinity to $0^{o}K$ according to equation (20) gives a value of -10.0 ± 1.1k cal.mole^{-1}.
Since

$$E' = E - D + Q$$

substituting values of 123k cal.mole^{-1} for the C-F bond energy(47) and 51.1k cal.mole^{-1} for the heat of adsorption of fluorine on platinum(36) gives

$$E = 61.9 \pm 1.1\text{k cal.mole}^{-1}.$$

The value of 61.9 ± 1.1k cal.mole^{-1} for the electron affinity of the C_4F_7 radical appears to be reasonable when compared with the measured electron affinities of other trigonal carbon radicals. Thus the electron affinity of C_6F_5 was found to be 63.3k cal.mole^{-1}.(39)

6.3.2 1700^{o} - $1800^{o}K$ region.

An apparent electron affinity of approximately -205k cal.mole^{-1} was observed in this temperature region. This behaviour is very similar to that observed with perfluorocyclobutane in this temperature region and is also ascribed to more extensive degradation on the filament.

6.4 Undecafluorocyclohexane.

Undecafluorocyclohexane supplied by the Imperial Smelting Corporation was allowed to evaporate into the magnetron apparatus with maintenance of the pressure at 1 X 10^{-3} mm Hg. Iridium filaments were used and ion and electron currents were measured over a filament temperature range of 1500° to 1850°K. Plots of the logarithm of the ratio of these currents versus reciprocal temperature showed two distinct regions corresponding to the temperature ranges 1500° to 1650°K and 1650° to 1800°K. Figure 13 shows a typical plot.

6.4.1 1500° to 1650°K region.

An apparent electron affinity of + 11.0 ± 1.7k cal.mole^{-1} was observed in this temperature region. The entropy change calculated from equation (28) was 79.1 e.u. This value is indicative of dissociative capture with adsorption. In this instance a hydrogen atom or a fluorine atom can be adsorbed.

$$C_6F_{11}H + e \rightarrow C_6F_{11}^{-} + H_{ads}$$

$$C_6F_{11}H + e \rightarrow C_6F_{10}H^{-} + F_{ads}$$

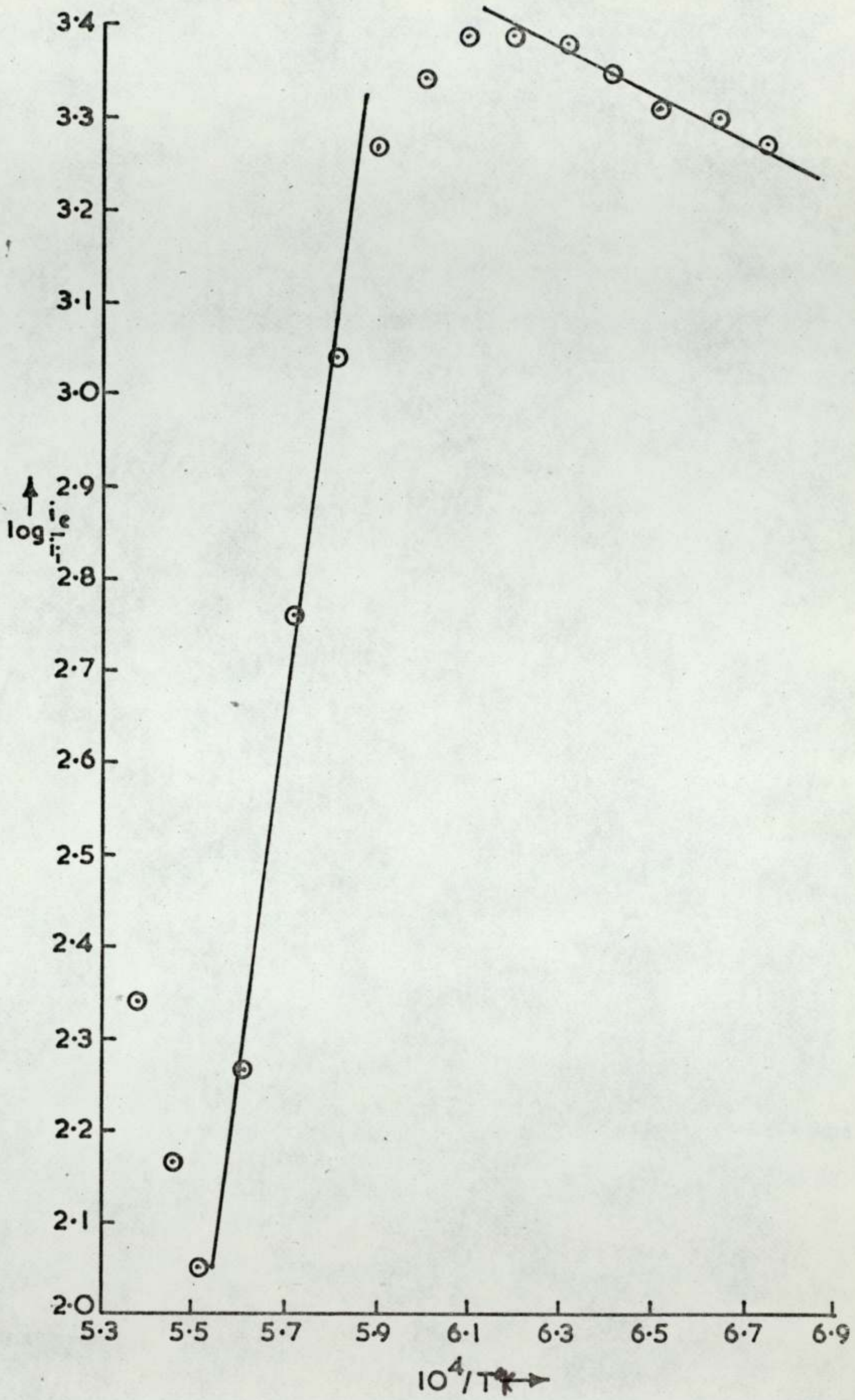


FIGURE 13

Ion-electron current ratios for $C_6F_{11}H$

The electron affinities of C_6F_{11} and $C_6F_{10}H$ would be expected to be similar, since the heats of adsorption of hydrogen and fluorine atoms on iridium are also similar. From considerations of energy the controlling influence on the hypothetical choice between the two reactions would be the difference in strength of the C-F and C-H bonds. The C-F bond is about 20k cal.mole^{-1} stronger than the C-H bond which thereby favours C-H bond scission. A consideration of the electron affinity of $C_6F_{10}H$ when the appropriate substitutions are made into the expression

$$E' = E - D + Q$$

lends support to this view because the value so obtained would be unreasonably high at 72.5 ± 1.7k cal.mole^{-1}. However, substituting a value of 102k cal.mole^{-1} for the $F_{11}C_6-H$ bond energy, 49k cal.mole^{-1} for the heat of adsorption of fluorine on iridium, and 1.5 ± 1.7k cal.mole^{-1} for the apparent electron affinity corrected according to equation (20) gives

$$E' = 37.5 \pm 1.7\text{k cal.mole}^{-1}$$

An electron affinity of 37.5 ± 1.7k cal.mole^{-1} for the C_6F_{11} radical compares reasonably with that obtained for CF_3 of 43.4k cal.mole^{-1}(36), both of which form tetrahedral carbanions.

6.4.2 1650° to 1800°K region

An apparent electron affinity of about -200k cal.mole^{-1} was observed in this temperature region. This behaviour resembles that of perfluorocyclobutane and of perfluorobutene - 2 in similar temperature regions. As before, this is ascribed to more extensive degradation on the filament.

6.5 Perfluorodecalin.

Perfluorodecalin supplied by the Imperial Smelting Corporation was allowed to evaporate into the magnetron apparatus. The pressure was maintained at 1 X 10^{-3} mm Hg. Iridium filaments were used and ion and electron currents were measured over the filament temperature range 1500° to 1800°K. The plots of the logarithm of the ratio of these currents versus reciprocal temperature showed two distinct regions corresponding to the temperature ranges 1500° to 1650°K and 1650° to 1800°K.

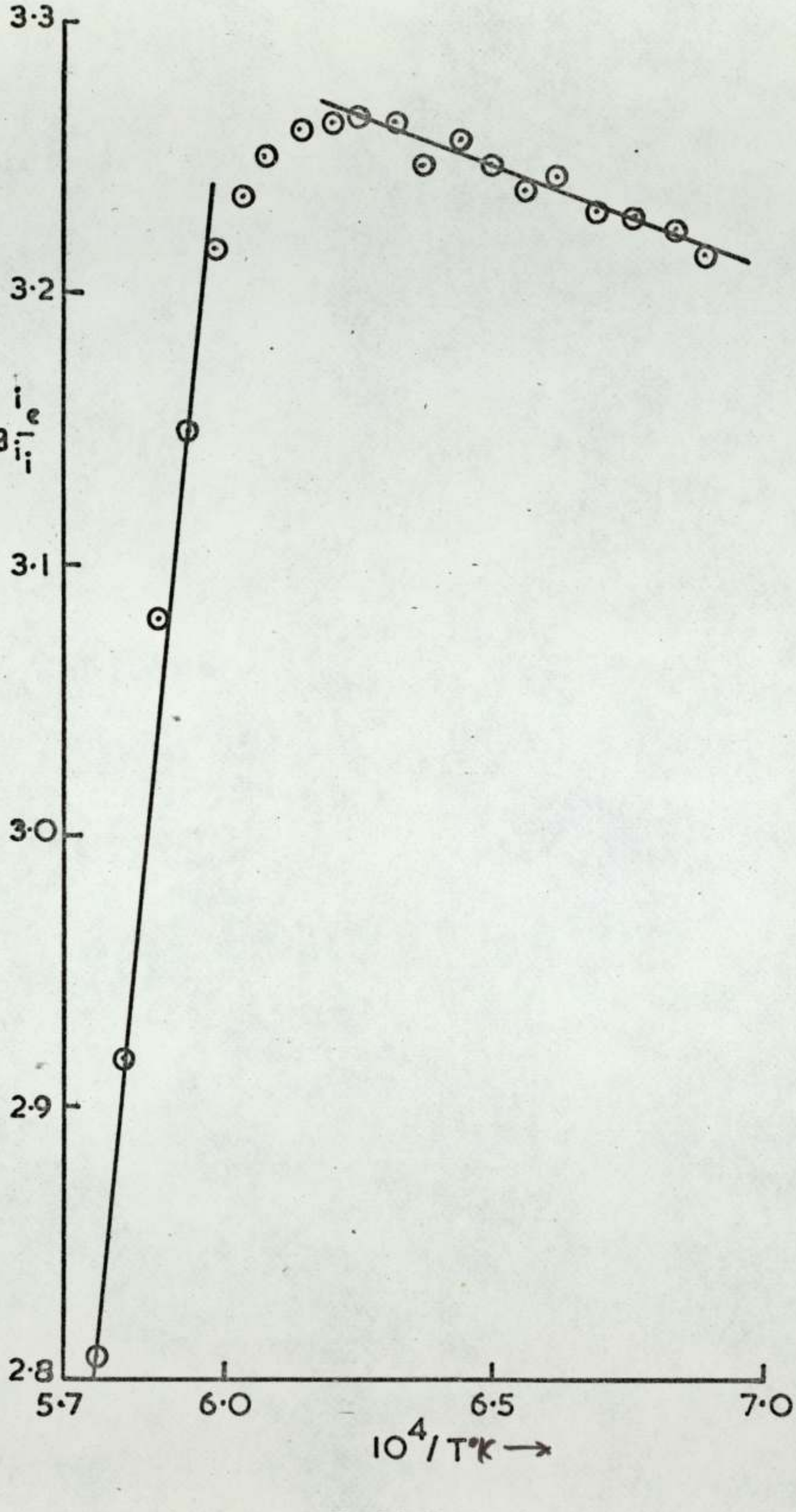


FIGURE 14

Ion-electron current ratios for $C_{10}F_{18}$

6.5.1 1500°to 1650°K region.

An apparent electron affinity of + 2.4 ± 5.3k cal.mole^{-1} was observed in this temperature region. The entropy change was calculated from equation (28) to be 72.4 e.u. This is indicative of a type 4 process of dissociative capture with adsorption. The following process could therefore be postulated:

$$C_{10}F_{18} + e \rightarrow C_{10}F_{17}^{-} + F_{ads}$$

The apparent electron affinity when corrected by equation (20) becomes -6.9 ± 5.3k cal.mole^{-1} at 0°K.

Since $E' = E - D + Q$

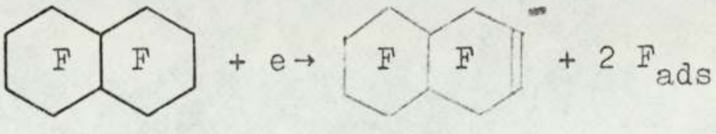
then substituting values, taking the C-F bond energy to be 120k cal.mole^{-1} and the heat of adsorption of fluorine on iridium to be 49k cal.mole^{-1}

$$E = 64.1 \pm 5.7\text{k cal.mole}^{-1}$$

However, a value of 64.1 ± 5.7k cal.mole^{-1} for the electron affinity of the $C_{10}F_{17}$ radical is unreasonably large when compared with that of other radicals giving tetrahedral carbanions. The behaviour which occurs is probably more complex than the simple dissociative capture with adsorption process considered here.

6.5.2 1650° to 1800°K region.

In this temperature region an apparent electron affinity of -102 ± 7k cal.mole^{-1} was observed. The entropy change from equation (28) is -75 e.u. These values indicate that a more complex behaviour is occurring than in the four types of process normally considered. Further degradation on the filament is therefore postulated, and is in accord with the interpretation of the large negative apparent electron affinities observed with perfluorocyclobutane, perfluorobutene - 2 and undecafluorocyclohexane in similar temperature regions. A process which appears feasible in this instance is the fission of two C-F bonds with adsorption of the fluorine atoms on the filament. The perfluorodecalene negative ion is then desorbed.



Classically this process involves a loss of nine degrees of freedom. A correction of 9/2RT gives an apparent electron affinity of -117.3 ± 7k cal.mole^{-1} at 0^{o}K.

Since

$$E' = E - 2D + 2Q$$

substituting values, taking D as 120k cal.mole^{-1} and Q as 49k cal.mole^{-1} gives

$$E = 24.7 \pm 7\text{k cal.mole}^{-1}.$$

Comparable experimental measurements are few, but a value of 24.7k cal.mole^{-1} for the electron affinity of perfluorodecalene appears reasonable. Hexafluorobenzene is somewhat similar and has an electron affinity of 27.6k cal.mole^{-1}(39).

6.6 Conclusions.

The fluorocarbon compounds examined in the magnetron all exhibited small or thermoneutral variations of the ion and electron current ratio with filament temperature in the 1500° to 1700°K range. The resulting small apparent electron affinity values were most satisfactorily interpreted in terms of loss of a fluorine atom, or, in the case of undecafluorocyclohexane, a hydrogen atom, which was adsorbed onto the filament. The resulting radical was then desorbed as a negative ion. Similar thermoneutral behaviour has been observed previously with several fluoro-aromatic compounds in the magnetron, and was also interpreted in terms of dissociative capture with adsorption(39).

With the exception of perfluoropropane, large negative values of the apparent electron affinity were obtained with the fluorocarbon compounds in the magnetron at higher filament temperatures in the 1700° to 1800°K region. This behaviour was attributed to more extensive reaction at the filament.

Perfluorocarbon negative ions have stabilities which generally are in the same range as those formed by the sulphur compounds examined. The sulphur pentafluoride negative ion has an exceptionally high stability, however, which was not equalled by any of the perfluorocarbon negative ions observed. There is a probable correlation between the electrical strength of a dielectric and the stability of the negative ions that it can form. It has been shown that the electron affinities of the radicals formed by dissociation of sulphur hexafluoride and perfluorocarbons are substantially higher than those of the undissociated molecules. Such high electron affinities may be a dominant influence on the electrical strength of these dielectric materials. Electrical breakdown of the dielectric is not an essential prerequisite for chemical breakdown of molecules of the dielectric, because chemical breakdown can result from the preceding electrical discharge phenomena. The electronegative dielectric can therefore inhibit the electron multiplication processes, essential for electrical breakdown, firstly by direct capture of electrons by molecules of the dielectric, and secondly by the dissociative capture of more energetic electrons. It is postulated that the latter process is of paramount importance in an explanation of the electrical strength and arc quenching properties of sulphur hexafluoride and perfluorocarbon dielectrics.

PART II

DISCHARGE DEGRADATION

7. INTRODUCTION

Perfluorocarbon fluids are becoming of increasing importance as electrical insulants and coolants where their properties of high electrical strength, high heat transfer efficiency, non-flammability, thermal stability and compatability with metals and insulators are of particular value. It is postulated that perfluorocarbons have an enhanced electrical strength due to the high stability of the negative ions that they can form. The attachment of free electrons may quench incipient electrical discharges. Nevertheless, when perfluorocarbons are subjected to sufficiently severe electrical stress such inhibitions are overcome and electrical breakdown occurs. It is inevitable that in their use as electrical insulants and coolants, overstressing of the perfluorocarbon fluid will occasionally occur. The resultant electrical breakdown will be accompanied by chemical reaction. Products of the chemical reaction may strongly affect subsequent performance of the fluid as an electrical insulant and may have other undesirable properties, for example they may be corrosive or toxic. It is of some practical importance, therefore, to establish the nature of the discharge degradation products formed by various perfluorocarbons.

Chemical phenomena induced by electrical discharges are not in general well understood, due both to their complexity and the lack of very extensive study. Indeed Kaufmann(58) states that "Our understanding of the chemistry of discharge processes is still in a rudimentary state; the field is more an art than a science, and thus represents one of the last frontiers of chemistry". In particular very little study has been directed towards the discharge chemistry of perfluorocarbons. In view of the practical relevance and academic interest, a study of the major chemical effects of electrical discharges on perfluorocarbons was undertaken and forms the major part of the work described in this dissertation.

8. GENERAL THEORETICAL CONSIDERATIONS

8.1 Types of electrical discharge and their production(56)(57).

Discharges are described by a wide variety of terms which relate to their appearance, by some aspect of the device by which they are produced, or by the name of a person associated with the discharge. This nomenclature has led to some confusion and requires some clarification.

In principle an electric discharge can be produced within a medium by the capacitive, inductive, or resistive coupling of a source of electrical power to the medium. Resistive coupling is achieved by the application of sufficient potential difference between electrodes in direct contact with the medium. Inductive and capacitive coupling do not require direct contact between the electrodes and the medium. Inductively-coupled discharges are produced by the generation of an electric field in the medium by the changing magnetic field from, in general, a microwave or radiofrequency power source. Capacitive coupling is achieved by the application of an alternating potential between electrodes separated from the medium by dielectric barriers. Oscillating electrostatic charges at the barriers allow a displacement current to flow through the medium.

Essentially the coupling of a source of electrical power to the medium by whatever means produces a plasma of electrons and positive ions. It is convenient to distinguish between only two types of plasma or discharge regimes: those of relatively low density, and those of relatively high density. A discharge of low plasma density does not raise the temperature of the medium far above ambient and can therefore be described as non-thermal. In gases at pressures below about 20 mm Hg such discharges are often termed glow discharges and have a diffuse appearance. At higher pressures the plasma tends to become more localized and striations can be observed. Such discharges are often termed high pressure glow, or corona particularly if associated with point electrodes, and are relatively non-thermal. A high density plasma produces local heating of the medium and can therefore be described as thermal. Arcs, sparks, and plasma jets are examples of the thermal discharge regime. It will be shown that the thermal or non-thermal nature of an electrical discharge governs its chemical effect.

8.2 Electron production and loss processes(58)(59).

The maintenance of an electric discharge depends upon a sufficient level of electron production to allow conductivity, and must be balanced by the electron loss processes. The major electron production process occurs in the bulk phase and is the production of secondary electrons by electron impact ionization

$$e + A \rightarrow 2e + A^+$$

Primary electrons are produced by background and cosmic radiation, and in the case of discharges generated by electrodes in direct contact with the bulk phase, by field emission, thermionic emission, and ion impact-induced emission from the cathode.

Electrons are lost from the discharge by ambipolar diffusion to the walls and by various recombination processes.

The major recombination process is dissociative recombination

$$e + AB^+ \rightarrow A + B$$

Three-body recombination is of lesser importance

$$A^+ + e + e \rightarrow A + e$$

Radiative recombination can occur, but at a negligible rate

$$A^+ + e \rightarrow A + h\nu$$

Electron loss by negative ion formation can occur by a three-body process

$$e + A + B \rightarrow A + B^-$$

and by dissociative attachment

$$e + AB \rightarrow A + B^-$$

Negative ion formation processes can be very fast and can compete effectively with dissociative recombination. The binding energy of the resulting negative ion is, however, much smaller than that of the neutral molecule and rapid electron detachment processes also operate e.g. associative detachment

$$A + B^- \rightarrow AB + e$$

The steady state concentration of negative ions is therefore small and their formation and decomposition processes are not generally important factors in the maintenance of the plasma balance.

8.3 Electron energies.

The distribution of electron energies in a discharge is calculable if only elastic collisions between molecules and electrons are considered. The calculated distribution is similar to the Maxwell-Boltzmann distribution although the high energy tail is relatively diminished. To a first approximation the electron distribution will be markedly affected by inelastic collisions between electrons and molecules producing excitation of rotational, vibrational, and electronic levels. Unfortunately, the calculation cannot take account of such collisions because the nature and cross-sections of these processes are largely unknown even for relatively simple substances. The extreme complexity of the discharge allows only a macroscopic description. Mean electron energies are generally considered to be about 2eV corresponding to an electron temperature of about 30000°K(59).

8.4 Electron excitation processes.

Only a very small proportion of the free electron population of the discharge in the high energy tail of the electron energy distribution curve has sufficient energy, usually above 10eV, to produce ionization by collision. Thresholds for electronic excitation are lower than those for ionization and cross-sections for electronic excitation rise more rapidly with electron energy than those for ionization. Electronic excitation processes consequently have considerably higher probabilities(59). Electronic excitation frequently leads directly or by dissociation to chemically active species. Despite the fundamental importance of ionization processes for the maintenance of the discharge, ionic processes can make only a very small contribution to the totality of discharge chemical phenomena. The major chemically important species in the non-thermal discharge are neutral excited molecules.

A probable excitation process is electron impact excitation vertically from the ground state to a radiative state of lifetime typically 10^{-8} seconds. If, however, the excitation energy is greater than the dissociation energy of the molecule, dissociation can occur in one of three principal modes(58)

(i) the upper state is repulsive and dissociates upon its first pseudo-vibration, i.e. within about 10^{-13}sec,

(ii) the upper state is bound, but the molecule is formed on a repulsive part of its potential energy curve at a point above its dissociation energy and will therefore dissociate on its first vibration also within 10^{-13}sec,

(iii) the upper state is bound and the molecule is formed with less than the dissociation energy for that state, but there is another state of lower dissociation energy with which the first state may interact. There is then some probability of pre-dissociation.

For electrons having relatively low energy, as are the bulk of those in electric discharges, there is also a high probability of electronic excitation by optically-forbidden non-vertical transitions(65). The cross-sections for forbidden transitions are sharply peaked and confined to narrow energy bands. Electrons at sufficiently low velocities can be involved in intermediate long-time interactions with molecules(63)(64). This considerably increases the probability of non-vertical transitions which require less energy than vertical transitions. The metastable states resulting from these optically forbidden transitions are of particular chemical importance. Since they cannot readily return to the ground state by photon emission, they have relatively long lifetimes and engage in collision processes. It is believed that such metastable neutral species can engage directly in chemical reactions which require more energy than is available to the ground state species. They may also dissociate to give free radicals. Unfortunately very little is known about the chemistry of excited species. This is a major factor in the uncertainty surrounding chemical processes in electrical discharges since in all probability the chemistry of non-thermal discharges is predominantly that of electronically excited neutral molecules.

The possible importance of vibrational excitation in discharge processes cannot be ruled out. Long-time interactions between low energy electrons can lead to direct vibrational excitation. Recent work(60) has shown that rates of vibrational excitation can be very large. Degradation of vibrational energy to translational energy is inefficient so that steady state concentrations of vibrationally excited molecules can be maintained at significant levels. The mechanism of direct vibrational excitation involves the formation of a virtual negative ion which decays to give the vibrationally excited molecule plus a slow electron(65). The involvement of a virtual negative ion state causes this process to be highly specific and to vary by two orders of magnitude from one molecule to another. This process may be of particular relevance to perfluorocarbon compounds by virtue of their electronegativity.

8.5 Discharge equilibria.

A major characteristic of the discharge is the large deviation of its energy partition from thermal equilibrium. The effective temperature of free electrons in the discharge is typically tens of thousands of °K, that of electronically or vibrationally excited states may be thousands of °K, whereas translational and rotational temperatures may be only tens or hundreds of °K above ambient in the non-thermal discharge(58). Energy distributions are probably sufficiently similar to Maxwell-Boltzmann for application of the temperature concept to be useful. Despite the temperature disequilibrium between the energy components of the system, discharge chemical reactions appear to show normal equilibrium behaviour. Thus a composition perturbation induced for example by the removal of a product from the reaction zone is compensated by an increase in the formation of that product. The yield is considerably increased(61) if, in the conversion of hydrogen and nitrogen to ammonia in the silent electric discharge, the ammonia is removed from the reaction zone as soon as it is formed by acid. Manes(62) has justified such behaviour by a statistical mechanical treatment of a model chemical reaction system in which energy is separately conserved within each degree of freedom of each species. The composition behaviour of such a system for any fixed set of energies can be shown to be the same as for a normal equilibrium system.

8.6 Comparison of the discharge environment with other chemically activating environments.

Some analogy may be apparent between the chemical effect of discharges and that of other chemically activating influences e.g. high temperatures, radiation etc. If such analogies can be drawn, an understanding of discharge chemical processes will be facilitated. The validity of any analogies will depend upon a knowledge of the relative contributions that particular forms of chemical activation make to the overall chemical changes observed.

8.6.1 Thermal activation.

The relevance of thermal processes to discharge chemistry will depend upon the translational temperatures achieved and on the extent of vibrational excitation.

Very high vibrational and translational temperatures are produced in thermal discharges, e.g. arcs, sparks, and induction plasmas. In a thermally-activated environment the density of thermally-activated species will be far greater than the density of electronically-activated species, and thermally-induced processes will therefore be expected to play the dominant role in the overall chemistry of the thermal discharge. There is evidence that this is the case. In a study of the formation of hydrogen cyanide from methane and nitrogen in a radiofrequency induction plasma, the experimental product compositions were found to be in agreement with predicted thermodynamic equilibrium computed by free energy minimisation(66). At the high translational temperatures which obtain in the thermal discharge, activation energies are available for most possible processes and, therefore, the plasma will tend to allow a thermodynamic equilibrium composition. The product composition obtained when the system is quenched to normal temperatures will, however, depend also on kinetic factors. As lower temperatures are reached, activation energies allowing a reversible reaction path for each product become unavailable. The following of a minimum free energy composition path is thereby kinetically restricted. The products of reactions requiring less activation will tend to be favoured in the quenched system, but the rate of quenching is an important limiting factor. To some extent concentrations of products at normal temperatures tend to correspond to thermodynamic equilibria at various higher temperatures where activation energies restricted further change(68).

The chemical effects of a thermal discharge are often broadly similar to pyrolysis. However, the product compositions from a thermal discharge are subject to the substantial effects that can be produced by differences in plasma temperatures, residence times, reactant mixing, temperature gradients, quenching time, and catalytic action.

Non-thermal discharges do not produce translational temperatures far above ambient. Chemical changes similar to those produced by pyrolysis are, therefore, not expected and not found in practice. Vibrationally-excited species can undergo reactions similar to those thermally induced, but such species are likely to be only a small proportion of the active species present in a non-thermal discharge. Non-thermal discharge products derive largely from electronically-excited molecules and are more similar to the products of reactions carried out at normal temperatures. In contrast thermal discharge products tend to be endothermic e.g. acetylene, hydrogen cyanide etc.

It can, therefore, be seen that the distinction between thermal and non-thermal discharges is of considerable use for the prediction and rationalization of broad chemical effects.

8.6.2 Radiolytic activation.

Irradiation with high energy electromagnetic radiation, e.g. X-rays, γ-rays, and by high energy particles e.g. neutrons, α particles, produce ionization within the target material. The major initiators of chemical change in all cases are the high energy electrons which such radiation generates. The chemical effects of irradiation are often largely independent, therefore, of the type of ionizing radiation used. Electrons of high energy are also the prime initiators of chemical change in the discharge and some comparability might be expected. The electron energy distribution in an irradiated medium is, however, considerably different to that in a discharge.

A large proportion of the free electrons in an irradiated system have energies considerably greater than the ionization potential of the medium. The discharge, by contrast, contains relatively few free electrons with energies above the ionization potential. An important consequence of this difference is that the ratio of ionization to excitation is considerably higher in the radiolytic system, although excitation processes are still numerically more important. Excitation produced by the high energy electrons in the radiolytic system may not correspond very closely to the excitation produced by the lower energy electrons of the discharge. Electrons of very high energy interact and excite in a very short time, and vertical transitions to optically allowed states are therefore favoured. Such excited species may dissociate by one of the previously described modes, or may return to the ground state by photon emission. It is unlikely that such species will have a sufficient life time to enter directly into collision processes.

The lower energy electrons typical of the discharge system will interact for longer times with molecules of the medium, and excitation is believed to be largely to optically forbidden states which are favoured by lower energy requirements. The metastable excited species will have a far longer lifetime and a different chemistry. This will often preclude a close correlation between the chemical effects of radiolysis and discharge. Direct vibrational excitation is similarly expected to be of lesser importance in radiolysis(65). Nevertheless for some substances several types of chemical activation e.g. pyrolysis, photolysis, and radiolysis give similar results(67) and this will probably extend to electric discharge also.

The X-ray irradiation of perfluorocyclobutane has been found to yield a very similar product distribution to that obtained using a low pressure electric discharge(70).

Despite the availability of more experimental data relating to the chemical effects of radiation, the chemical processes that occur are not well understood in detail and, as in discharge chemistry, the relative importance of ionic, radical, and molecular processes is still an area of controversy. Both systems have in common a complexity which precludes microscopic description.

The chemical effect of high temperature radiolysis is similar to pyrolysis(69) and, therefore, to the thermal discharge, because thermal activation dominates activation by electronic excitation.

8.6.3. Mass spectrometry.

The fragmentation of molecules by electron impact in the mass spectrometer is essentially a form of radiolysis. However, unlike most other radiolysis experiments, it is normally carried out at pressures sufficiently low to preclude reactions between the fragments and the non-fragmented parent molecules.

Furthermore, information concerning the fragmentation processes is only obtained in terms of the positive or, less commonly, negative ions which are sufficiently stable to be separated and measured. It is clearly difficult to relate an electron impact mass spectrum to the major primary fragmentation process that occurs. The fragmentation of a neutral molecule which is of interest in discharge chemistry will probably be quite different to that of the parent positive or negative ion because electron distributions and therefore bond orders will be different. As a consequence, analogy between mass spectra and discharge chemistry is unlikely to be fruitful.

The relationship between pyrolysis and mass spectra has been examined by Bentley and Johnstone(106) who concluded that there was little evidence to suggest this particular analogy.

8.7 Reaction types of possible importance in the discharge.

8.7.1 Ionic

Many mass spectrometric studies of ionic reactions have been carried out, and the more important types are now well known. Most of these will occur to some extent in the discharge. Direct sampling of the ions present in discharges by means of a probe coupled to a mass spectrometer has been undertaken by several workers and has given some understanding of ionic processes in the discharge.

Ion formation processes.

Negative ion formation by resonance capture can occur at low electron energies of 0-7eV and can therefore be the major ionization process in the discharge.

$$XY + e \rightarrow XY^{-} \begin{array}{l} \nearrow X + Y^{-} \\ \searrow Y + X^{-} \end{array}$$

Negative ion populations tend to be small, however, due to their high decomposition rates, as mentioned previously.

At higher electron energies, positive and negative ions are readily formed:

$$\begin{array}{lcl} XY + e & \rightarrow & X^{+} + Y^{-} + e \\ & \rightarrow & X^{-} + Y^{+} + e \\ & \rightarrow & XY^{+} + 2e \\ XY^{+} & \rightarrow & X^{+} + Y \\ & \rightarrow & Y^{+} + X \end{array}$$

Ion-molecule reactions

Atom transfer e.g.(71)

$$CH_4^+ + C_3H_6 \rightarrow CH_5^+ + C_3H_5$$

Symmetrical transfer e.g.(73)

$$\begin{aligned} C_2H_4^+ + C_2H_4 &\rightarrow C_3H_5^+ + CH_3 \\ &\rightarrow C_4H_7^+ + H \end{aligned}$$

Positive ion transfer e.g.(72)

$$C_2H_6^+ + H_2O \rightarrow C_2H_5 + H_3O^+$$

Negative ion transfer e.g.(74)

$$C_2H_5^+ + C_3H_8 \rightarrow C_2H_6 + C_3H_7^+$$

Charge transfer e.g.(75)

$$H^+ + H_2 \rightarrow H_2^+ + H$$

Neutralization e.g.(76)(77)

$$NO^+ + NO_2^- \rightarrow NO + NO_2$$

$$NO^+ + NO_2^- + M \rightarrow NO + NO_2 + M$$

Electron detachment e.g.(76)

$$O^- + H_2 \rightarrow H_2O + e$$

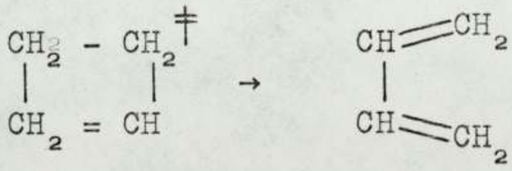
Ion-molecule reactions often have high rate constants e.g. $10^{-9} cm^3 mol^{-1} sec^{-1}$. Little or no activation energy is often required. Despite the efficiency of these reactions, there is little evidence that they contribute significantly to the totality of chemical phenomena. This is because ionic concentrations will be low relative to those of other active species.

8.7.2 Molecular

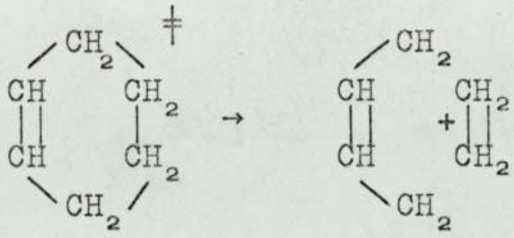
(a) Vibrationally excited molecules.

Many unimolecular processes giving non-radical products are known e.g.

Isomerisation



Dissociation



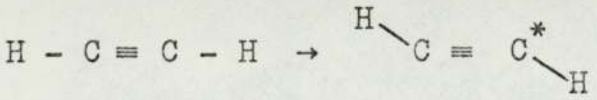
Elimination

$$C_2H_5Cl^{\ddagger} \rightarrow CH_2 = CH_2 + HCl$$

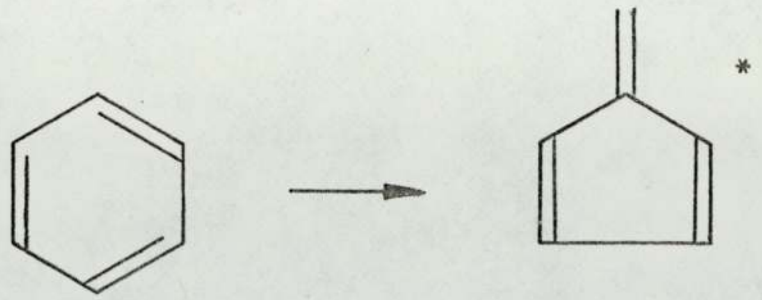
Alternative homolytic fission processes giving free radicals can occur at higher degrees of vibrational excitation, but in non-thermal discharges the lower energy processes are likely to be more favourable.

(b) <u>Electronically excited molecules</u>.

Electron transitions from bonding orbitals to non-bonding or anti-bonding orbitals have a large effect on the orbital symmetry of the molecule. Bond orders may be considerably different and their relative orientation changed with respect to the ground state. In some few instances such changes in bond orientation have been observed spectroscopically e.g.



$$H - C \equiv C - H \rightarrow \overset{H}{\diagdown} C = C^{*} \underset{H}{\diagdown}$$



Excited molecules usually contain longer, weaker bonds than in the ground state, giving an increased reactivity. Reactions can occur involving excited molecules that would not be feasible for ground state molecules. The excited molecule can therefore be physically and chemically different from the ground state molecule and from other excited states of the same molecule. Very little is known concerning the structure and chemistry of most excited molecules. Molecules in optically-allowed excited states may decay by photon emission, and molecules in optically-allowed or forbidden states may decay by dissociation to radical or molecular products, or by isomerization. Recent vacuum photolysis work(98) has indicated that dissociation to molecular species is more important than better-known dissociation to radicals.

The reactions of electronically-excited molecules, particularly metastable excited molecules, are expected to contribute substantially to the overall chemical change produced by a non-thermal discharge. The paucity of experimental data and theoretical rationale in this area contributes largely to the difficulty of interpretation of non-thermal discharge chemistry.

(c) Free radical.

Electronically-excited molecules often dissociate to give free radicals and this process will probably be the major mode of their formation in the non-thermal discharge. In the thermal discharge, however, the homolytic dissociation of highly vibrationally-excited molecules will be the major source of free radicals. Free radicals have often been considered(78) to be the most important chemical intermediates in electrical discharge processes. However, since many radical propagation and termination processes can be readily envisaged, it is often possible to devise a radical scheme that will account for the observed products irrespective of whether or not they actually arise in this manner. The ability to reconcile product distributions in terms of possible radical processes cannot be taken as evidence that such radical processes actually occur. The relative importance of radical processes compared with molecular processes is not clear in discharge chemistry or in radiolysis. Radical scavengers are often used in an attempt to differentiate between the radical and molecular processes. The results of such experiments are often ambiguous.

Several workers have shown that radical scavengers can be involved in more complex reaction sequences than was originally thought. The very small steady state concentrations of free radicals render their estimation by other means very difficult.

8.8. The role of surface reactions in discharge chemistry.

Surface catalytic processes can govern product formation in an electrical discharge. Thus, for example, the production of hydrogen atoms by a radiofrequency electrodeless discharge in a clean borosilicate glass vessel occurs by dissociation of hydrogen molecules to the extent of about 10%. If several % of oxygen is added the dissociation of hydrogen can increase to about 50%. Operation of the discharge in pure oxygen for several minutes, followed by pure hydrogen, gives a dissociation to hydrogen atoms of 90% and continues to operate at a similarly high level for several hours. Clearly, the oxygen discharge modifies the surface in such a manner as to inhibit recombination of hydrogen atoms(59). Catalytic effects observed with small quantities of impurities or additives are generally the result of surface modification and not homogeneous catalysis(58).

Discharge products are often formed by heterogeneous recombination and are susceptible to surface conditions. Equilibria in the discharge can be modified by surface control of condensation, recombination and the quenching of active species.

Differentiation between homogeneous and heterogeneous discharge processes is clearly necessary for an understanding of the chemistry of a discharge system.

9. PREVIOUS STUDIES OF PERFLUOROCARBON DEGRADATION

A limited amount of experimental study of the degradation of perfluorocarbons has been carried out by various workers. Degradation resulting from thermal, radiolytic, electron impact, and discharge activation of perfluorocarbons is reviewed.

9.1 Thermal degradation

The pyrolysis of several perfluorocarbons at a platinum filament in a gold plated vessel has been examined (79). Filament temperatures in the range 1050° to 1450°C were used with substrate pressures of 100 to 500 mm Hg. Thermal stabilities were observed to be in the order:

$$CF_4 > C_2F_6 > \text{cyclic} - C_5F_{10} >> C_3F_8 \simeq n - C_4F_{10} >> C_2F_4 > n\text{-}C_5F_{12}$$

The platinum filament catalysed the pyrolysis. Carbon-carbon bonds were ruptured in preference to carbon-fluorine bonds to give saturated and unsaturated products of lower molecular weight, and some polymeric product in addition. Radical processes involving $CF_2:$ were postulated.

The thermal decomposition of perfluorocyclobutane has been well studied and found to proceed by a first order unimolecular process (48) (49).

$$c-C_4F_8 \rightarrow 2\ C_2F_4$$

The activation energy of this process was 74.3k cal.mole^{-1}. In parallel with this process, but with an activation energy of 87k cal.mole^{-1}, dissociation also occurred as follows:

$$c-C_4F_8 \rightarrow C_3F_6 + CF_2:$$

The dissociation of perfluoroethylene to give difluorocarbene, and its own subsequent dissociation,has been studied in the shock tube (82).

$$C_2F_4 \rightarrow 2\ CF_2:$$

$$CF_2: \rightarrow CF\cdot + F\cdot$$

Above 1800°K perfluoroethylene was completely dissociated to difluorocarbene, which was itself dissociated from 2600°K. The dissociation of perfluoroethane in the shock tube has been studied in the temperature range 1300° to 1600°K at 4 atmospheres pressure(83).

$$C_2F_6 \rightarrow 2\ CF_3 \cdot$$

9.2 Radiolysis

The γ-radiolysis of C_2F_6 has been studied in some detail (84)(85)(86). CF_4 is a major product together with some C_3F_8 and C_4F_{10}. The formation of perfluoroalkenes was not observed; this is compatible with photochemical evidence (87) which suggests that disproportionation of perfluoroalkyl radicals is improbable. Perfluoroalkenes have been suggested as possible intermediates which are subsequently consumed, but this appears unlikely. Loss of molecular fluorine from perfluorocarbons is thermodynamically unfavourable, unlike loss of hydrogen from hydrocarbons. Similarly, fluorine atom abstraction from a perfluorocarbon by a fluorine atom is not favourable because the C-F bond is considerably stronger than the F-F bond. As a consequence molecular fluorine has not been observed as a product of perfluorocarbon radiolysis.

The probability of cleavage of a C-F bond and a C-C bond appears to be similar in radiolysis. The radiolysis of several saturated perfluorocarbons has been carried out using pile radiation. The products were all saturated and of higher and lower molecular weight than the parent compound(89). Radical schemes can be formulated which account for the products obtained. Experiments using oxygen as a radical scavenger indicate that radical reactions may be important in radiolysis. The irradiation of several unsaturated perfluorocarbons resulted in a large degree of conversion to unsaturated polymeric material. The radiolysis of perfluoropropene yielded trimers and tetramers containing the $CF_2 = CF -$ and $-CF \neq CF -$ groups and some cyclic structures (90). Other workers have found that C_3F_6, cyclic - C_4F_6, and C_4F_8, give liquid or waxy unsaturated trimers and tetramers(91). Perfluorobenzene yields almost exclusively a solid polymer(89). Dewar perfluorobenzene has also been reported as a product of the γ-radiolysis of perfluorobenzene(92). Such valence tautomers, which have also been observed in photochemical studies, can decay to the ground state or can polymerize. Even at elevated temperatures perfluorobenzene, perfluorobiphenyl, perfluoronapthalene, and perfluoro-o-terphenyl are converted almost exclusively to solid polymer(93).

Radical processes are generally considered to be very important in such conversions. Although disproportionation of perfluoroalkyl radicals is not in general believed to occur, it has been suggested for some cyclic species at 350° - $400^{\circ}C$ (94). The disproportionation of substituted phenyl radicals has also been suggested (95). Fluorine atoms are believed to act as intermediates in the radiolysis of perfluorocarbons but have not been detected directly.

9.3. Electron impact

The positive ion mass spectra of many perfluorocarbon compounds have been published. Nevertheless most of the perfluorocarbons studied in the course of the present work were subjected to 70 eV electron impact in an AEI MS9 mass spectrometer; the fragmentation patterns so obtained are of interest for comparison with other degradative regimes.

9.3.1 Straight chain perfluoroalkanes.

CF_4 , C_2F_6 , C_3F_8 , C_5F_{12}, and C_6F_{14} were examined. In each case the most abundant ion was CF_3^+, followed by $C_2F_5^+$, and then $C_3F_7^+$. The parent ions were not observed. The major primary dissociation would appear to involve scission of the terminal carbon-carbon bond.

9.3.2 Straight chain perfluoroalkenes.

C_3F_6, C_4F_8 - 2-ene and C_7F_{14} - 1-ene were examined. The major ion was $C_3F_5^+$, followed by CF_3^+. Parent ions were observable, and the double bond therefore stabilizes the ion with respect to its saturated analogue.

9.3.3 Saturated alicyclic perfluorocarbons.

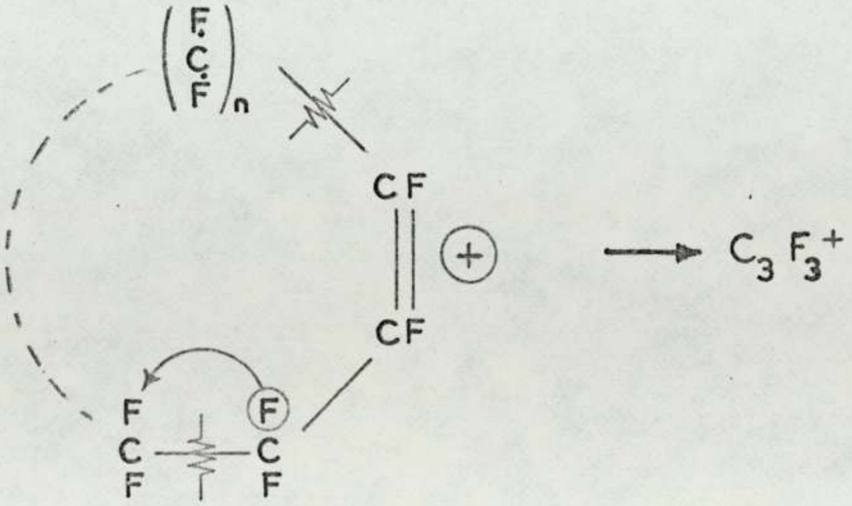
Cyclic-C_4F_8 , C_6F_{12}, and bicyclic -$C_{10}F_{18}$ were examined. No uniform fragmentation pattern was observed, although in all cases CF_3^+ and $C_3F_5^+$ were important ions. $C_2F_4^+$ was the major ion from cyclic-C_4F_8 but was of lesser importance from cyclic-C_6F_{12} and bicyclic-$C_{10}F_{18}$. Parent ions were not observed. Obviously the formation of CF_3^+ requires a re-arrangement process.

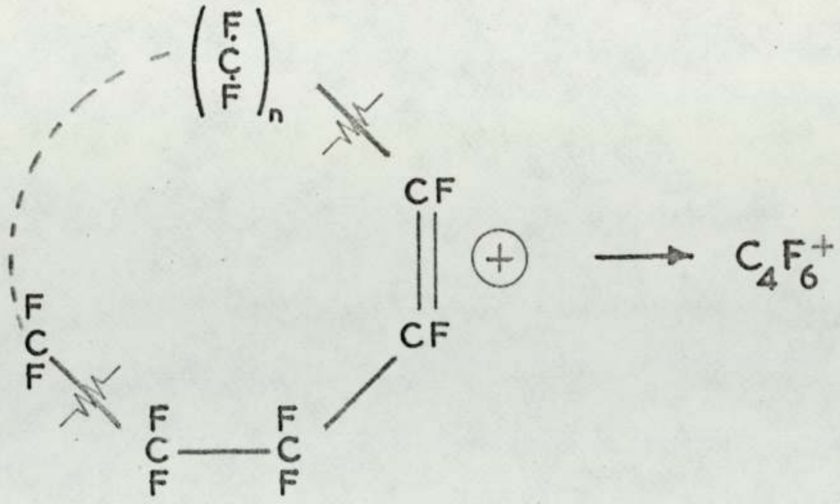
9.3.4 Saturated alicyclic perfluorocarbons with side chain perfluoromethyl groups.

Cyclic $-C_4F_6(CF_3)_2$, cyclic $-C_6F_{10}(CF_3)_2$, and bicyclic $C_{10}F_{17}(CF_3)$ were examined. No common fragmentation pattern was observed but CF_3^+ was important in all cases. Cyclic $-C_4F_6(CF_3)_2$ gave $C_2F_4^+$ as the major ion cf. cyclic $-C_4F_8$, but this was of minor importance for the other two compounds. Parent ions were not observed.

9.3.5 Alicyclic perfluoroalkenes.

Cyclic $-C_4F_6$, C_5F_8, and C_6F_{10} were examined. Although no common fragmentation pattern was observed, $C_3F_3^+$ and $C_4F_6^+$ were important in all cases. Notably, CF_3^+ was only of minor importance. Parent ions were observed cf. straight chain perfluoroalkenes. The most important process thus appeared to be





An important conclusion that can be drawn from the electron impact fragmentation patterns, and that may be relevant to other degradation processes, is that deposition of a relatively large amount of energy in a molecule does not preclude the structure of the molecule from strongly influencing the resulting mode of dissociation. The relative stability of the various possible fragment ions that can be formed is a co-influence.

9.4 Discharge degradation.

Very little published work is available concerning the chemical effects of electrical discharges on perfluorocarbons. However, in a study of the X-radiolysis of perfluorocyclobutane, it was found that the substitution of a tesla-coil discharge between stainless steel electrodes for the X-ray source gave identical fragmentation$^{(96)}$. The products observed in this study were perfloroethylene, perfluoropropylene, perfluoropropane, and more than ten C_5 to C_{14} products. A white PTFE-like polymer was also formed. Perfluoromethane may have been formed but was not measured. The higher molecular weight products appeared to contain one or two cyclobutane rings. The addition of oxygen or ethylene to the system eliminated all products with the exception of perfluoroethylene. This was interpreted as a strong indication that radical processes were of major importance. Three main breakdown paths were postulated.

(i) Direct dissociation to give C_2F_4

(ii) Dissociation to a perfluorocyclobutyl radical and a fluorine atom.

(iii) Dissociation to give C_3 and C_1 species,

i.e.

$$\begin{aligned} c - C_4F_8 &\rightarrow 2C_2F_4 \\ &\rightarrow c - C_4F_7\cdot + F\cdot \\ &\rightarrow CF_3\cdot + CF_2 = CF - CF_2\cdot \end{aligned}$$

The observed products could be rationalized in terms of these processes followed by radical propagation and termination.

10. EXPERIMENTAL

Table 1 lists a wide range of perfluorocarbon compounds which were subjected to thermal and non-thermal discharges. Those insulants and coolants available commercially and known as Flutec PP$^{(R)}$ fluorocarbon liquids are marked with an asterisk.

(R) Imperial Smelting Corporation.

Table 1

Compound	Supplier
Perfluoromethane	British Drug Houses Limited
Perfluoroethane	British Drug Houses Limited
Perfluoropropane	Ozark Mahoning Company
Perfluoropropene	British Drug Houses Limited
Perfluorobutene - 2	Cambrian Chemicals Limited
Perfluorobutyne - 2	Pierce Chemical Company
Perfluorocyclobutane	Cambrian Chemicals Limited
Perfluorocyclobutene	Pierce Chemical Company
Perfluoropentane*	Imperial Smelting Corp.
Perfluorocyclopentene	Pierce Chemical Company
Perfluorohexane*	Imperial Smelting Corp.
Perfluorocyclohexane	Imperial Smelting Corp.
Perfluorocyclohexene	Imperial Smelting Corp.
Perfluorodimethylcyclobutane	Pierce Chemical Company
Perfluorobenzene	Imperial Smelting Corp.
Perfluoroheptene - 1	Pierce Chemical Company
Perfluoromethylcyclohexane*	Imperial Smelting Corp.
Perfluorodimethylcyclohexane*	Imperial Smelting Corp.
Perfluorodecalin	Imperial Smelting Corp.
Perfluoromethyldecalin*	Imperial Smelting Corp.

Before use, these compounds were all analysed by gas chromatography and mass spectrometry. Some compounds were also examined for the presence of hydrogen-containing impurities by proton magnetic resonance spectroscopy. The purity of most perfluorocarbons was found to be good, although some contained isomeric impurities. Only the perflurobenzene contained hydrogenic impurities.

The perfluorocarbons were subjected to thermal discharge by the generation of sparks and arcs between electrodes. Non-thermal discharges were generated capacitively in an apparatus of the Siemens type. Product analysis was then carried out, principally by gas-solid chromatography, and enabled some aspects of the basic chemical processes occurring in a perfluorocarbon discharge to be deduced.

10.1 Product analysis.

The qualitative and quantitative analysis of perfluorocarbon discharge products could be most satisfactorily achieved by gas chromatography. A Varian Aerograph Series 1200 gas chromatograph fitted with a flame ionization detector was used. The output from the detector was recorded by a 1mV Honeywell Electronik 15 chart recorder.

Published work suggests the use of various gas chromatographic column liquid phases for the separation of perfluorocarbons. Many of these liquid phases were examined; however, none was as effective as the purely solid phase column packings available commercially under the names Phasepak P and Phasepak Q. These materials are cross-linked polystyrene beads; the P and Q denotes different degrees of cross linking. Twelve foot by one eighth inch diameter columns were packed with 85-100 mesh Phasepak P or Phasepak Q. The Phasepak Q columns were found to give very good separation of C_1 to C_8 perfluorocarbons, whilst the Phasepak P columns gave a good separation of C_6 to C_{18} perfluorocarbons. Nitrogen carrier gas was used at a flow rate of 25 ml min^{-1}.

Good peak shapes for product mixtures covering a wide range of molecular weights were recorded within reasonable analysis times by the use of temperature programming at $4^{o}C\ min^{-1}$. Compared to the more commonly-used liquid phase on a solid support, the advantage of a purely solid phase chromatographic column packing is that it avoids a gradual alteration in separation characteristics due to loss of liquid phase and consequent higher background ionization level. Solid chromatographic media are also capable of stronger interaction with very volatile compounds and are therefore more suitable for their separation than are liquid media.

Standards corresponding to all the major products of the discharge degradation of perfluorocarbons were available and allowed identification and quantitative analysis of the components of the product mixtures to be effected. The elution temperature versus carbon number curves for homologous series were regular as shown in figures 15 and 16 . This allowed the tentative identification by interpolation of several minor products for which standards were not available for comparison. The presence of carbon-carbon double bonds increased column retention relative to analogous saturated perfluorocarbons. It was also noted that the peak width of perfluoroalkenes were significantly smaller than those of perfluoroalkanes after allowing for retention time-related broadening. This effect was an additional aid to tentative identification. It is known that unsaturated perfluorocarbons are often capable of forming complexes with unsaturated hydrocarbons(80)(81). Therefore it is probable that the increased retention of perfluoroalkenes, and their smaller peak widths, are both a result of interaction between the π-electrons of the double bond of the perfluoroalkene and those of the polystyrene column packing.

The most important products were generally of low molecular weight with one to three carbon atoms. Clearly the number of possible compounds in this carbon number range is severely restricted. As the elution of perfluorocarbons occurred in order of carbon number with

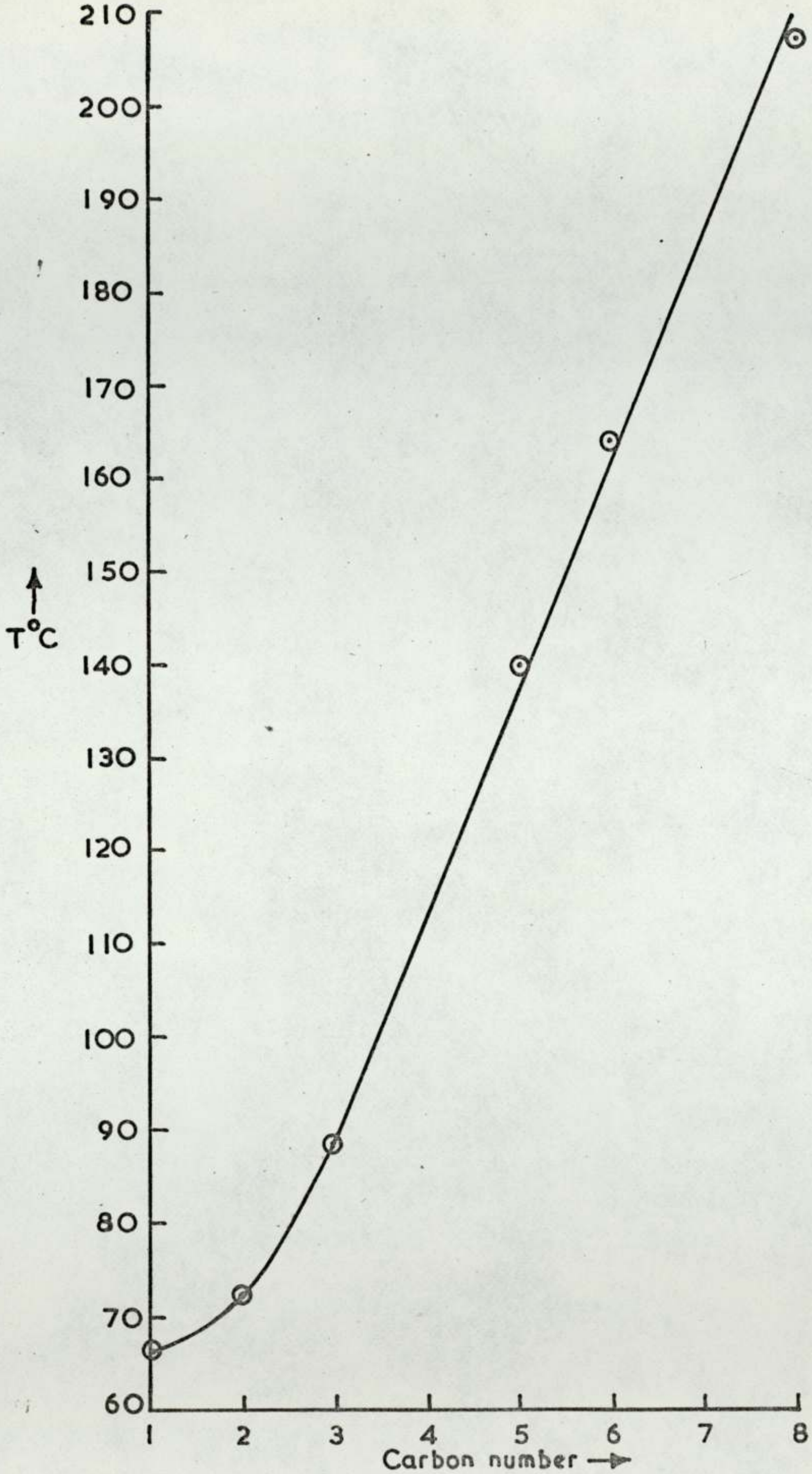


FIGURE 15

Elution of perfluoroalkanes from Phasepak Q column temperature programmed at 4°C min^{-1}

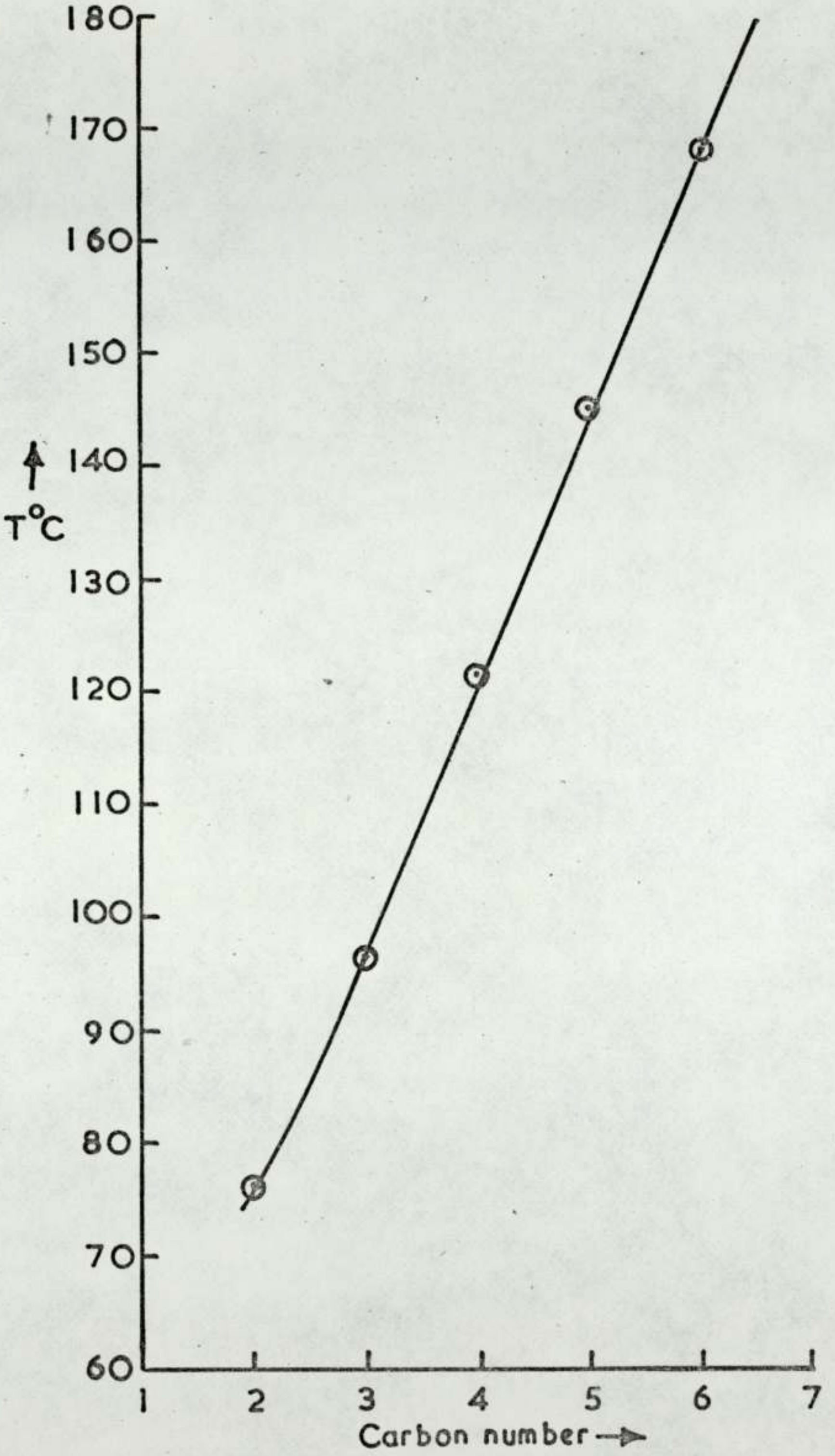


FIGURE 16

Elution of perfluoroalkenes from Phasepak Q column temperature programmed at 4°C min^{-1}

good resolution, the possibility of error due to overlap or to the coincident elution of more than one compound was much lower than is usual in gas chromatographic analysis. Furthermore, hydrocarbons, partially fluorinated hydrocarbons, and oxygen-containing compounds were all eluted after the most important perfluorocarbon products.

The identity of the perfluoroalkenes C_2F_4 and C_3F_6, which were often very important products, was confirmed by addition of bromine to discharge product mixtures when the peaks assigned to these compounds diminished. The rate of bromination of C_2F_4 was observed to be quite fast whilst that of C_3F_6 was slow enough to be measured by taking samples at intervals for gas chromatographic analysis. The rates of bromination were in accord with published data and hence provided additional evidence of identity.

Most possible saturated and unsaturated perfluorocarbons of carbon numbers one to four appeared to be present in some discharge product mixtures even if only to a very minor extent, but no chromatographic peak was observed that could be assigned to C_2F_2. However C_2F_2 is known to polymerize spontaneously at room temperature (104) and may be present only transitorily.

The use of a fast scanning mass spectrometer coupled to a gas chromatograph would have been an ideal system for the measurement and identification of perfluorocarbon degradation products. However, the cost of such a system was prohibitive and, in view of the power of the gas chromatographic system used, was clearly not essential.

Polymeric products not amenable to gas chromatographic analysis were also obtained in many cases. These were isolated by distillation of volatile material from the polymeric residue. Extraction of this residue with perfluorohexane, or other organic solvents, enabled an oily or waxy yellow-brown polymer to be separated from a black solid polymer resembling soot. These polymers were subjected to elemental analysis. The oily or waxy polymer usually had a stoichiometry of approximately C_6F_{10} and the infra-red analysis indicated a general similarity to PTFE but with a degree of carbon-carbon double bond unsaturation. The soot-like polymer had a stoichiometry of approximately C_6F_3 which compares with approximately C_8H for soot of hydrocarbon origin.

10.2 The response of the flame ionization detector to perfluorocarbons

Flame ionization detection (FID) is widely used in quantitative gas chromatographic analysis of organic compounds because it is sensitive and has a wide range of linear response. The FID response to an organic compound depends upon its constitution, provided that operating conditions are fixed. Variations in detector geometry or gas flow rates can alter the

TABLE 2

Relative response to FID

COMPOUND	RELATIVE MOLAR RESPONSE
Perfluoromethane	0.025
Perfluoroethane	2.0
Perfluoroethylene	18
Perfluoropropane	8.6
Perfluoropropene	31
Perfluorobutene - 2	42
Perfluorobutyne - 2	69
Perfluorocyclobutane	15
Perfluorocyclobutene	49
Perfluoropentane	33
Perfluorocyclopentene	83
Perfluorohexane	50
Perfluorocyclohexane	110
Perfluorocyclohexene	130
Perfluorodimethylcyclobutane	62
Perfluorobenzene	250
Perfluoroheptene - 1	95
Perfluorodimethylpentane	83
Perfluoromethylcyclohexane	89
Perfluoro-octane	84
Perfluorodimethylcyclohexane	110
Perfluorodecalin	140
Perfluoromethyldecalin	170

relative and absolute FID response. For an accurate quantitative analysis it is essential to establish the response of the FID to the compounds to be measured under the conditions to be used. Standard mixtures of all the perfluorocarbons available were prepared and samples subjected to gas chromatographic analysis. The FID response to the components of the standard mixture was then calculated from planimetric measurements of the peak areas obtained. Table 2 lists the relative response values determined in this manner.

The FID response to organic compounds is reliably attributed to the chemi-ionization reaction (115)(116):

$$CH + O \rightarrow CHO^{+} + e$$

There is a low probability of a carbon atom in an organic compound forming a CH radial, and only about one carbon atom in 10^{5} is converted to CHO^{+}. Nevertheless this is sufficient for flame ionization quantitation to be a very sensitive technique. Since each carbon atom has some probability of undergoing the chemi-ionization reaction, the molar FID response is additively related to the number of carbon atoms contained in a molecule. Consequently it has proved useful for comparative and predictive purposes to consider organic compounds in terms of the single carbon atom moieties obtained by scission of all carbon-carbon bonds. These moieties are commonly assigned effective carbon response values determined by an empirical analysis of relative molar response $^{(117) - (120)}$. Such values are usually related to a base of 100 for the CH_n group of an alkane. The effective carbon response values show how the response attributable to a particular carbon atom is affected by the atoms to which it is attached. A similar analysis of the tabulated perfluorocarbon response data shows that the response attributable to a carbon atom depends primarily on the number of fluorine atoms to which it is attached. The order of effective carbon response is

$$C \sim CF > CF_2 > CF_3 >> CF_4$$

This result is quite different to that obtained with hydrocarbons where the effective carbon response of a CH_n group is independent of n. Clearly, the formation of CH radicals from CF_n groups entails the preliminary stripping of fluorine atoms. However, thermal dissociation of CF_n groups in the hydrogen-air flame will not occur readily due to the high C - F bond energy of about 120kcal.mole^{-1}, the probability of formation of a CH radical is thereby reduced. The concept of partial- or non-participation of carbon atoms which are in groups capable of forming chemically- and thermally stable entities has been recognised. Thus it is envisaged that the very low effective carbon response values for the $-O-CH_2$, $-COOH$, and $\geqslant C-N <$ groups is due to their facile conversion to HCHO, CO_2, and $-C \equiv N$ respectively. The extent of formation of such entities can depend on the mechanism of pyrolysis which depends in turn on molecular structure.

The apparently anomalous molar response of some O- and N-containing compounds can be rationalized by invoking specific pyrolysis mechanisms.(120) In some other instances, for example in the variations of molar response of alkyl nitrites and nitroalkanes with structure, no definite trends were apparent. It is probable in such cases that the relation between molar response and structure is complicated by the occurrence of alternative pyrolysis mechanisms, some of which may occur in parallel. Similarly, the molar responses of perfluorocarbons are not wholly amenable to a simple rationalization whereby CF_n groups can be assigned effective carbon response values which can be universally applied. Unknown mechanistic factors are clearly of importance. It is evident that the response attributable to a CF_n group is primarily dependent on n, but as a consequence the molar response is sensitive to any redistribution of fluorine atoms occurring prior to or during pyrolysis.

An additional structure-related factor that could operate is in complete pyrolysis. This argument has been advanced to explain the low anomolous response of some high molecular weight hydrocarbon materials (101) (102); the high thermal stability of perfluorocarbons would clearly predispose them to this behaviour, but no trends towards lower response with increased molecular weight were observed.

Typical values for the relative contributions of CF_n moieties to FID response are 30, 10, 1 and 0.03 for n = 1, 2, 3, and 4 respectively. The probability of complete stripping of fluorine atoms allowing a finite probability of formation of CHO^+ is thus in inverse exponential proportion to n. This is indicative of a stepwise process where the rate of each step is limited by its energy requirements. It is known that the chemi-ionization process is restricted to a narrow zone of the inner flame cone where temperatures rise rapidly from ambient to over 1000°C. Residence times in this zone are obviously short. A posssible stepwise process for loss of fluorine atoms is

$$CF_n + H \rightarrow CF_{n-1} + HF$$

Molecular hydrogen can successively replace fluorine atoms by hydrogen atoms:

$$CF_n + H_2 \rightarrow CF_{n-1}H + HF$$

The CH_n moieties, in common with those of hydrocarbon origin, have then a probability of undergoing chemi-ionization, via CH, independently of n. The reaction with molecular hydrogen will be statistically favoured with respect to the reaction with atomic hydrogen because the inner cone of the hydrogen-air flame contains a higher concentration of molecular hydrogen than atomic hydrogen.

11. THERMAL DISCHARGE STUDIES

11.1 The apparatus

11.1.1 The electrical power sources

D.C. sparking experiments were carried out using a unit manufactured by Witton Electronics Ltd. This transformed the mains supply and rectified it to give a maximum of 20kV at 10mA, which charged a pair of parallel 0.0005 μ F capacitors. The capacitors discharged to earth between suitably spaced electrodes in the perfluorocarbon liquid or gas to produce sparks. Using point-plane electrode geometry at spacings of about 2mm, the rate of discharge of the capacitors was typically about fifty times per second drawing a current of about 2mA at 10-20kV.

A.C. arc experiments were carried out using the 240 volt 50 Hertz mains supply transformed to a maximum of 15kV at 17mA. The transformer was manufactured by Foster Ltd.

11.1.2 The thermal discharge cells

The cell construction material

The material chosen for construction of the discharge cells was polytetrafluoroethylene (PTFE). This had many advantages over other possible materials.

A material having excellent insulating properties was essential and PTFE is one of the best insulators available. The hydrophobic nature of the surface of PTFE prevents adsorption of moisture which can allow high voltage tracking. The absence of adsorbed moisture is also of great chemical importance because ambiguity can arise as a result of reactions with water at the walls when glass and silica vessels are used for discharge reactions. The PTFE surface is also very resistant to chemical attack and has a very low catalytic activity. The use of a material composed of the same elements as the reactants prevented the incorporation of other elements into the products by wall reactions and also limited the possible wall reactions that could occur. In particular, PTFE is already saturated with respect to fluorine and is therefore inactive towards any fluorine formed by the discharge; most other materials would react with fluorine. Thus hydrocarbon polymers are unsuitable because of the high affinity of fluorine for hydrogen. The dense impermeable nature of PTFE reduces absorption relative to hydrocarbon polymers. Any contamination that might occur due to absorbed material from a previous experiment can be readily eliminated by baking the cell at 250°C.

Cell design

The cells constructed for discharges in liquid perfluorocarbons were of a small capacity, about 4ml, due to the high cost and scarcity of many perfluorocarbons. The cells consisted of a cylinder and end pieces which screwed in and carried the electrodes, as shown in figure 17.

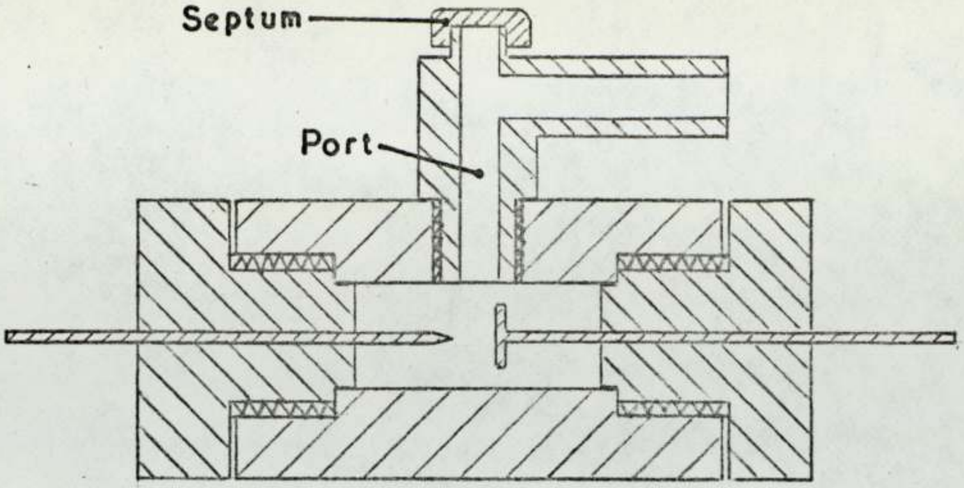


FIGURE 17
Static discharge cell

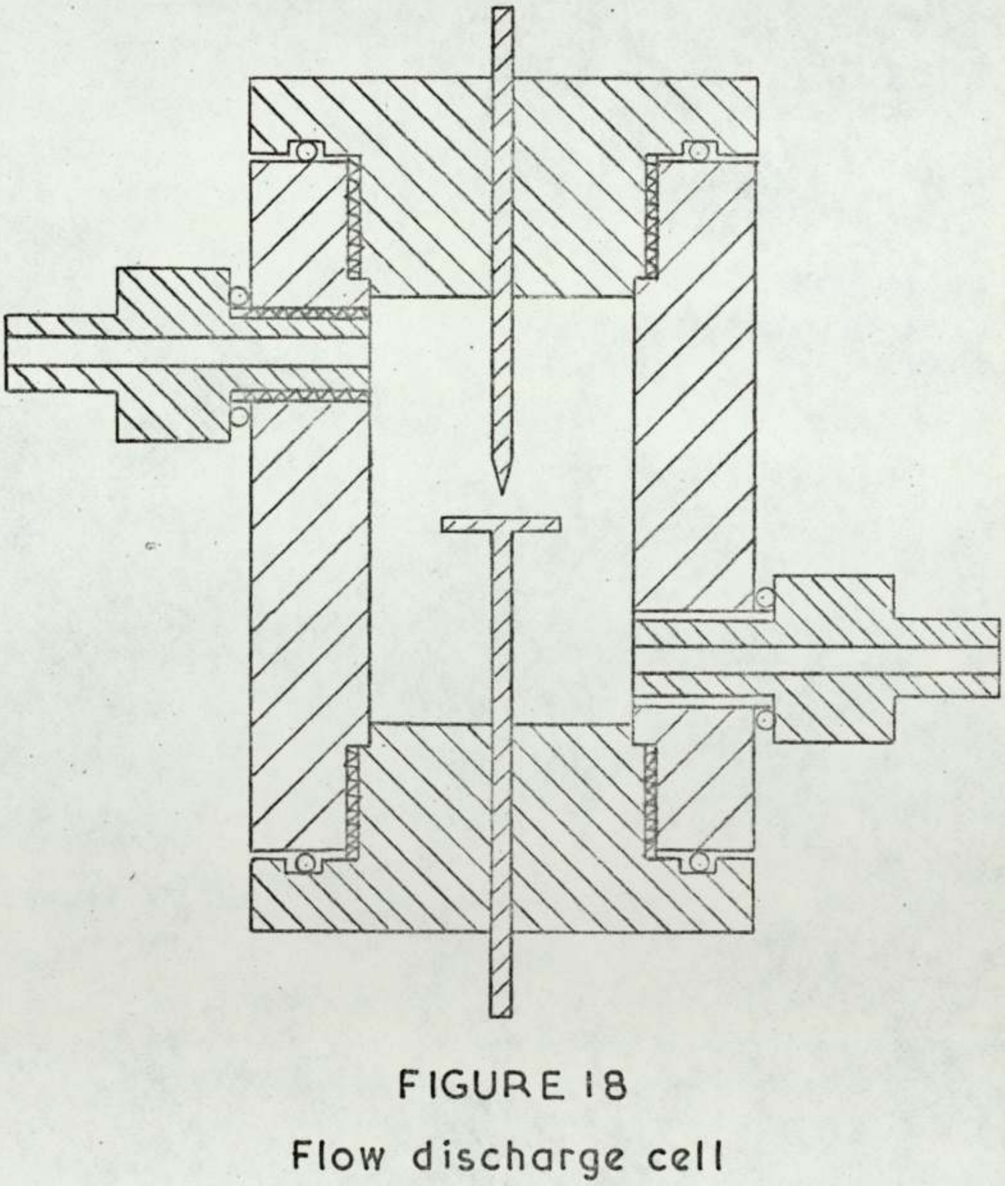


FIGURE 18
Flow discharge cell

Filling, degassing, and sampling operations could be carried out by virtue of an orifice in the cylinder, which also permitted control of volume and pressure.

A static system was not convenient for discharge experiments with gases and vapours, so a flow cell of about 20ml capacity was constructed for this purpose as shown in figure 18 .

Electrodes

Stainless steel point-plane geometry electrodes were used in the majority of experiments. The advantage of point-plane geometry is that breakdown occurs at larger electrode separations than with plane-plane, sphere-sphere, or point-point geometry provided that, in the d.c. system, point negative,plane positive polarity is used. The electrode separations used were generally 1.5 to 3.0mm.

Brass and aluminium were also investigated as electrode materials. It was considered to be a possibility that the nature of the electrode material might influence some chemical processes in the discharge, particularly surface processes. However, using conditions identical in all other respects, no differences in product composition could be detected when electrodes of different materials were used. The amount of metal vaporized was measured by weighing the electrodes before and after use, but by comparison with the amount of chemical change produced in the perfluorocarbon, the amount of vaporized material was negligible.

The probable conversion of the vaporized metal to the fluoride would not affect the product composition to an observable extent.

Variation of other electrode parameters such as the separation or the reversal of d.c. polarity did not appear to influence product composition.

11.2 Experimental procedure

11.2.1 Preparation of the cell

The cell components were thoroughly cleaned to remove polymeric deposits, washed with perfluorohexane, and baked at 250°C before use. After baking, the components were allowed to cool over phosphorus pentoxide in a desiccator. It was frequently necessary to grind and polish the electrodes because the point electrode rapidly became blunt and the plane electrode became pitted. The cell was then assembled and the electrode separation set with the use of a micrometer gauge. Pressurization with an inert gas was used to check that the cell was leak-tight.

11.2.2 Experiments with liquids

Liquid perflurocarbons were pre-treated by passing them through a column of molecular sieve to remove any moisture present, and then through a porosity 5 sintered glass filter to remove solid particles.

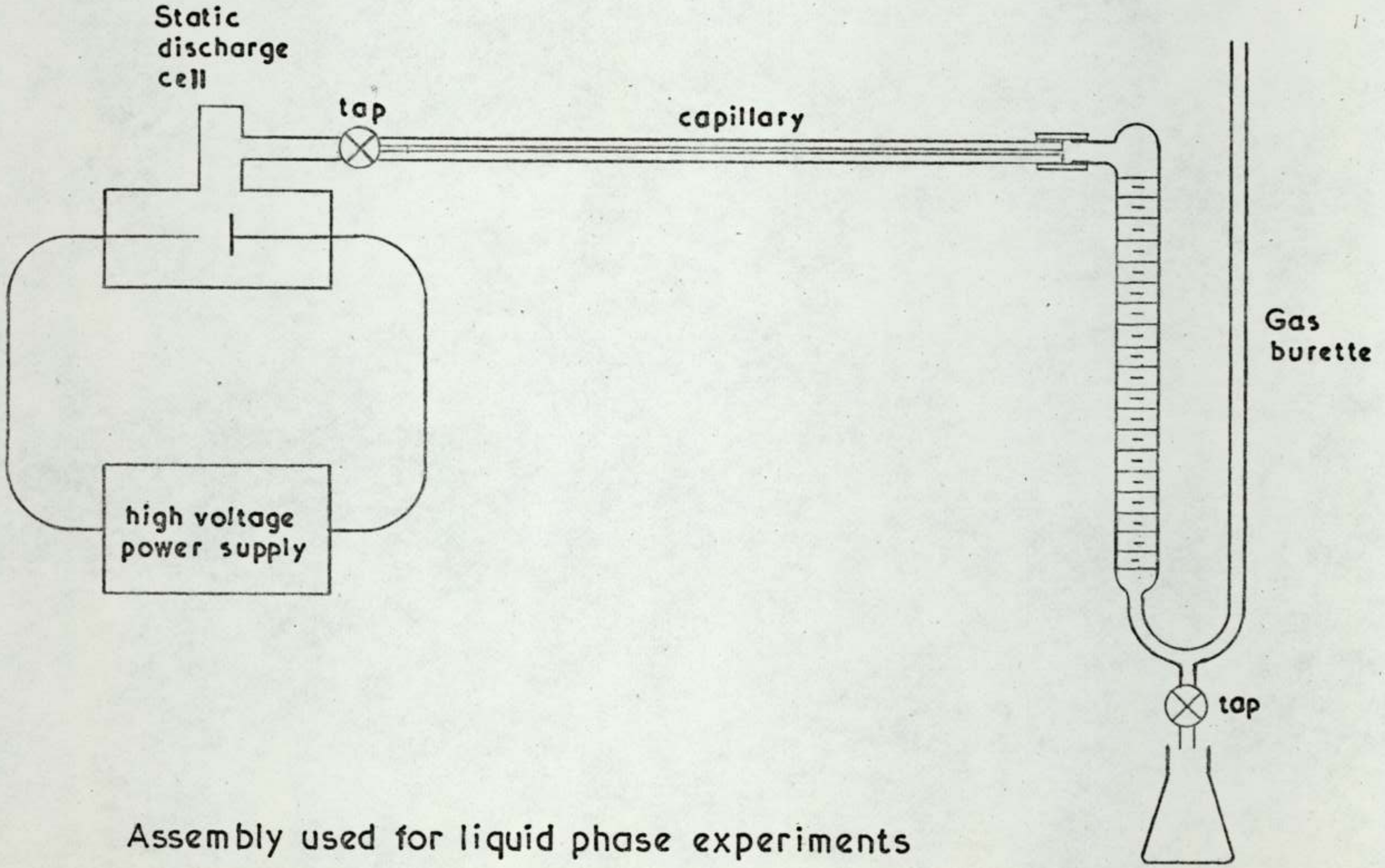
Figure 19 shows the assembly used for sparking and arcing experiments with liquids. The cell was connected to a sampling/filling port and, via a glass capillary, to a mercury gas burette. The perfluorocarbon liquid was passed into the cell through a syringe needle. Air was removed from the apparatus and from the liquid by flushing with an inert gas, introduced into the liquid via a needle passed through a septum on the port.

Sparking or arcing was then carried out for a timed period. Evolution of gaseous products accompanied the discharge. Atmospheric pressure was maintained within the apparatus by running mercury from the gas burette at an equal rate. Known fractions of the liquid and gaseous phases were then sampled through the septum by syringe and subjected to gas chromatographic analysis.

11.2.3 Experiments with gases and vapours

Gases were passed from their cylinders via flow meters into the flow cell where they were subjected to arcing or sparking. The exit gases were passed through a mercury non-return valve to prevent entry of air into the system. A septum allowed the exit gases to be sampled by syringe before venting to the atmosphere. The sample was immediately subjected to gas chromatographic analysis.

The vapours of liquids having satisfactory vapour pressures at normal temperatures were passed



Assembly used for liquid phase experiments

FIGURE 19

into the flow cell by inert carrier gases. This was effected by placing a small quantity of the liquid in a saturator as shown in figure 20 . An inert carrier gas was passed through the saturator where, in traversing the liquid in the form of small bubbles, it became saturated with the vapour of the liquid. Lower concentrations of the vapour in the carrier gas could be achieved by cooling the saturator or by subsequent dilution with more inert gas. The vapour and carrier gas was then passed through the flow cell and subjected to sparking or arcing followed by gas chromatographic analysis.

11.3 Product compositions produced by thermal discharge

11.3.1 The effect of flow rate and carrier gases

It was of crucial importance to establish whether the flow rates of gases or carrier gas-vapour mixtures through the flow cell could influence product compositions, and also whether the inert carrier gases could have any chemical effects.

Conversion to products was found to be inversely proportional to flow rate, indicating that the degradation process is not restricted by back reactions.

Experiments with mixtures of perfluorocarbon gases with the inert gases, He, Ne, and Kr, in various proportions showed that the degree of conversion to products, and the product compositions, were unaffected

Table 3 Part (i)

Product compositions obtained by thermal discharge

Parent Compound	C_2F_6	C_3F_8	C_3F_6	n-C_4F_6	c-C_4F_8	C_4F_8-2
Product	Molar percentage of total product yield					
CF_4	55	30	2.3	4.5	1.0	3.2
C_2F_4	31	42	86	55	91	65
C_2F_6		27	7.6	20	2.8	12
C_3F_6	0.9	1.5		*	3.9	13
C_3F_8	2.1		1.0	1.2	0.6	1.9
c-C_4F_8						
trans-C_4F_8-2			0.2	0.2		
cis-C_4F_8-2			0.2	0.9		
C_4F_8-1						
C_4F_{10}						
$[C_6F_{10}]_n$	1.0					
$[C_6F_3]_n$			3.0	18	1.0	3.8

* Not determined; peak masked by parent.

Table 3 Part (ii)

Product compositions obtained by thermal discharge

Parent Compound	c-C_5F_8 (v)	n-C_5F_{12} (v)	n-C_5F_{12} (ℓ)	n-C_6F_{14} (v)	n-C_6F_{14} (ℓ)
Product	Molar percentage of total product yield				
CF_4	2.0	11	11	11	22
C_2F_4	65	56	42	70	48
C_2F_6	4.7	20	19	12	13
C_3F_6	6.2	4.4	9	4.5	11
C_3F_8	0.8	5.7	19	2.9	3.7
c-C_4F_8	0.6	0.2		0.4	0.7
trans-C_4F_8-2	5.2			0.3	0.4
cis-C_4F_8-2					0.2
C_4F_8-1	2.8			0.1	0.2
C_4F_{10}	0.5	2.5		0.2	0.5
C_5F_{10}				0.1	0.4
$\left[C_6F_{10}\right]_n$			0.1		0.2
$\left[C_6F_3\right]_n$	13		0.2		0.3

Table 3 Part (iii)

Product compositions obtained by thermal discharge

Parent Compound	c-C_6F_{10}(v)	c-C_6F_{10}(ℓ)	c-C_6F_{12}(v)	c-C_6F_6(v)	c-C_6F_6(ℓ)
Product	Molar percentage of total product yield				
CF_4		4.3	2.3		
C_2F_4	77	63	85	41	38
C_2F_6	3.2	6.6	4.8	3.2	0.9
C_3F_6	3.6	5.0	2.6	10	1.2
C_3F_8			1.5	0.7	
c-C_4F_6	0.9		0.1		
c-C_4F_8	0.5	1.1	0.5		
trans-C_4F_8-2	2.9		0.3	0.6	
cis-C_4F_8-2		2.3		0.6	
C_4F_8-1	1.0				
C_5F_{10}	0.8				
c-C_6F_8					10.3
$\left[C_6F_{10}\right]_n$		4.2			5
$\left[C_6F_3\right]_n$	10	12	2.3	44	45

Table 3 Part (iv)

Product compositions obtained by thermal discharge

Parent Compound	$c\text{-}C_4F_6(CF_3)_{2(v)}$	$c\text{-}C_4F_6(CF_3)_{2(\ell)}$	$c\text{-}C_6F_{11}CF_3\ (\ell)$	$c\text{-}C_6F_{10}(CF_3)_2\ (\ell)$
Product	Molar percentage of total product yield			
CF_4	2.9	9.7	23	23
C_2F_4	55	29	46	26
C_2F_6	3.8	8.5	6.6	21
C_3F_6	33	44	10	18
C_3F_8	0.7	1.2	1.1	3.6
$c\text{-}C_4F_6$		2.6	0.1	
$c\text{-}C_4F_8$			1.0	
trans-C_4F_8-2	1.6	2.0	0.1	0.3
cis-C_4F_8-2	1.1		0.2	0.6
C_4F_8-1			0.1	0.9
C_5F_{10}			0.1	1.0
$c\text{-}C_6F_{12}$			15	1.8
$[C_6F_{10}]_n$		0.4	1.4	2.4
$[C_6F_3]_n$	2.0	2.3	4.5	8.8

Table 3 Part (v)

Product compositions obtained by thermal discharge

Parent Compound	C_7F_{14}-1(v)	$C_{10}F_{18}(\ell)$	$C_{11}F_{20}(\ell)$
Product	Molar percentage of total product yield		
CF_4	16	22	17
C_2F_4	42	42	43
C_2F_6	12	12	13
C_3F_6	7.8	8.4	10
C_3F_8	3.4	2.2	2.6
c-C_4F_8	0.4		
trans-C_4F_8-2	0.8		0.1
cis -C_4F_8-2		1.3	0.7
C_4F_8-1	0.8		0.2
C_4F_{10}		0.7	0.4
C_5F_{10}		0.7	0.4
C_6F_{10}		1.3	1.8
$\left[C_6F_{10}\right]n$	17	2.5	2.4
$\left[C_6F_3\right]n$		7.5	7.0

by the presence of the inert gas. This indicates that energy transfer processes involving inert gas species are not important in controlling the direction of thermal discharge reactions.

11.3.2 Product compositions from d.c. sparking in the gaseous and vapour phase

The results of the d.c. sparking experiments obtained using the flow system are given in table 3 and expressed in terms of molar percentage of total product yield. Polymeric products have, for comparative purposes, been calculated for as C_6F_{10} and C_6F_3. The results correspond to conversions of 1 to 2% of the parent compound. The flow rates necessary to achieve these conversions were dependent upon the dilution of the perfluorocarbon and upon its structure, but were typically about 30ml min^{-1}.

11.3.3 Product compositions from d.c. sparking in the liquid phase.

The results of the d.c. sparking experiments obtained using the liquid cell are also given in table 3 and are expressed in a similar manner to the gaseous and vapour phase results. These results correspond to conversions of 0.5 to 1% and were achieved in a sparking time of about 15 seconds typically, although the time was structure-dependent. The relative stability of perfluorocarbons towards thermal

Table 4

Relative stability towards thermal discharge

Compound	Stability*
CF_4	1200
C_2F_6	15
C_3F_8	13
c-C_4F_8	100
C_4F_8-2-ene	30
c-C_4F_6	25
n-C_4F_6	40
n-C_5F_{12}	20
n-C_6F_{14}	20
c-C_6F_{12}	45
c-C_6F_{10}	25
c-C_6F_6	50
c-$C_6F_{11}.CF_3$	40
C_7F_{16} -1-ene	35
$C_{10}F_{18}$	40

*Relative to arbitary value of 100 for c-C_4F_8

discharge degradation is given in table 4.

11.3.4 Product compositions produced by a.c. arcing

With conditions in other respects identical to those used in the d.c. spark experiments, liquid, gaseous, and vapour phase experiments were conducted using the a.c. power source. The d.c. sparks were of short duration, of the order of milliseconds, whereas the a.c. source produced a continuous arc. The power dissipated in unit time, and the rate of conversion to products, appeared to be fairly similar, however.

Despite the difference between sparks and a continuous arc, product compositions for perfluorocarbons which do not give rise to very much soot were almost identical. For most purposes the arc is simply a spark of long duration. Perfluorocarbons for which soot is an important product when subjected to sparking gave proportionally less soot when subjected to arcing and the proportions of their other degradation products were correspondingly altered. In particular the relative amount of waxy polymer increased, possibly indicating that the two main types of polymerization process are in competition. It was notable that perfluorohexane did not give any soot when subjected to a.c. arcing, whereas a small amount is formed by d.c. sparking. Although quantitatively this difference is not important, visually the effect is dramatic, and

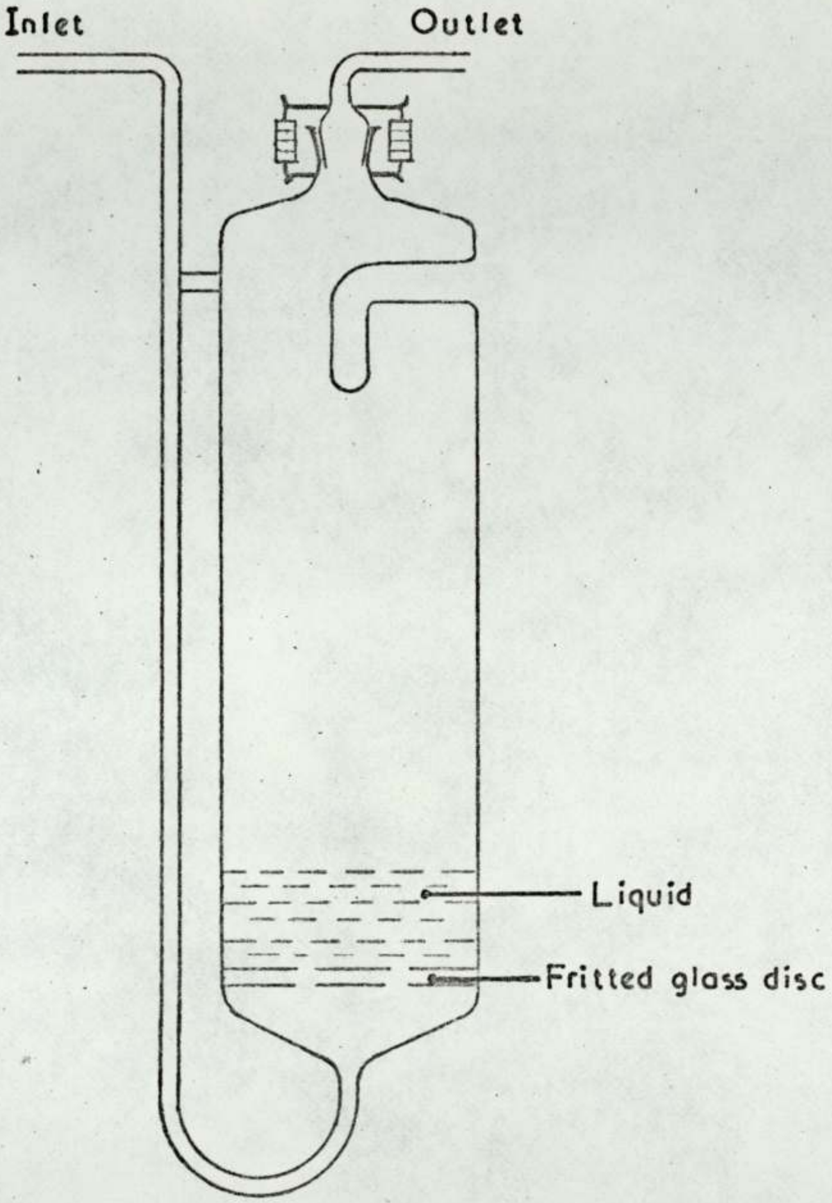


FIGURE 20

Saturator

has important consequences for electrical insulation. Soot particles, once formed, aid subsequent breakdown by their deposition on surfaces allowing high voltage tracking. An additional effect is that soot particles tend to be drawn into high field regions and can then give rise to a bridging effect.

It was considered a possibility that conditions in the a.c. arc might be less conducive to the initiation of soot particles than to their subsequent growth. A small amount of soot from a d.c. experiment was added to perfluorocyclohexane which was then subjected to a.c. arcing. However, this did not result in the formation of more soot . A lack of initiation of particle formation is therefore probably not the inhibitory factor.

11.4 The effect of the presence of other compounds on thermal discharge product distributions

11.4.1 Nitric oxide

Nitric oxide has the ability to scavenge free radicals and has been widely used in radiolysis and pyrolysis studies for the estimation of the extent of radical reactions. It is usually assumed that nitric oxide will terminate radical chains but will not enter into non-radical processes.

A maximum inhibitory effect is normally

produced by concentrations of several per cent, and the degree of inhibition produced is usually considered to represent the contribution of free radical reactions to the degradation process; residual reaction is considered to be non-radical. If this reasoning holds, nitric oxide scavenging can be of great mechanistic utility.

However it has been demonstrated in several instances that the interaction of nitric oxide with a system undergoing degradation is more complex than originally envisaged. Thus it has been shown that nitric oxide also takes part in radical initiation processes in alkane pyrolysis and that, despite only partial inhibition in the presence of nitric oxide, the pyrolysis is completely radical in nature. In practice it is seldom possible to draw unequivocal conclusions from the results of scavenging experiments.

Nitric oxide was added to perfluorocarbon gases and vapours in various proportions and the mixtures were subjected to d.c. sparking or a.c. arcing. Gas chromatographic analysis was then carried out in the usual manner. Unfortunately, masking of the CF_4 peak occurred in the presence of nitric oxide. However, it could be seen that perfluoroalkene products were reduced in yield in direct proportion to nitric oxide concentration, except where the parent compound was itself a perfluoroalkene. This indicated that the perfluoroalkenes were attacked directly by nitric oxide. Moreover, large concentrations of nitric oxide were necessary, about 20% , to produce a reduction in yields of perfluoroalkene products of 50%. It is therefore possible that the reactive entity was in fact atomic oxygen liberated from the nitric oxide by the action of the discharge.

Nevertheless nitric oxide is known to react with perfluoroalkenes at room temperature to form the nitronitroso and dinitro derivatives (113).

The presence of nitric oxide at low concentrations strongly affected the yield of waxy polymer and indicates that it is formed by a radical polymerization process.

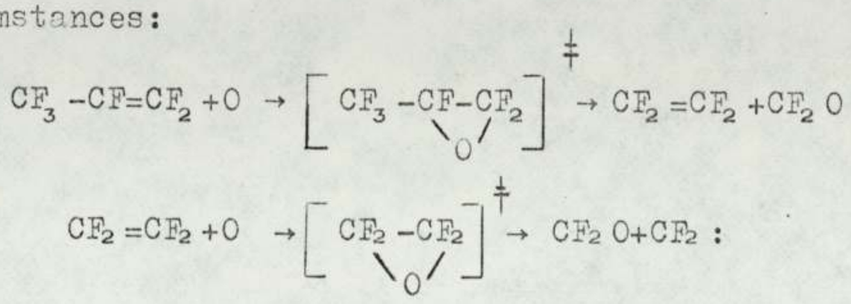
The yield of soot was not affected by small concentrations of nitric oxide however, and was only reduced by large concentrations. This effect could be attributed as in the case of perfluoroalkenes to attack by liberated oxygen atoms.

The thermal discharge is not an ideal system in which to conduct radical scavenging because, unlike for example a radiolytic system, it is highly inhomogeneous. Plasma regions are produced in which chemical activation is intense and in which the active species, which may well be radicals, will considerably outnumber the scavenging species. Radical scavenging ideally requires a low steady-state concentration of radical species and an excess amount of the scavenger.

In conclusion it is deduced that the waxy polymer is formed by radical processes occurring beyond the thermal discharge plasma. It is not possible to draw an unambiguous conclusion concerning the reduction in yields of perfluoroalkene products and 'soot' with large concentrations of nitric oxide, since this could be due either to attack of their radical precursors if any, by nitric oxide or liberated oxygen atoms in the plasma, or to attack by these species on the non-radical formed products in or beyond the plasma.

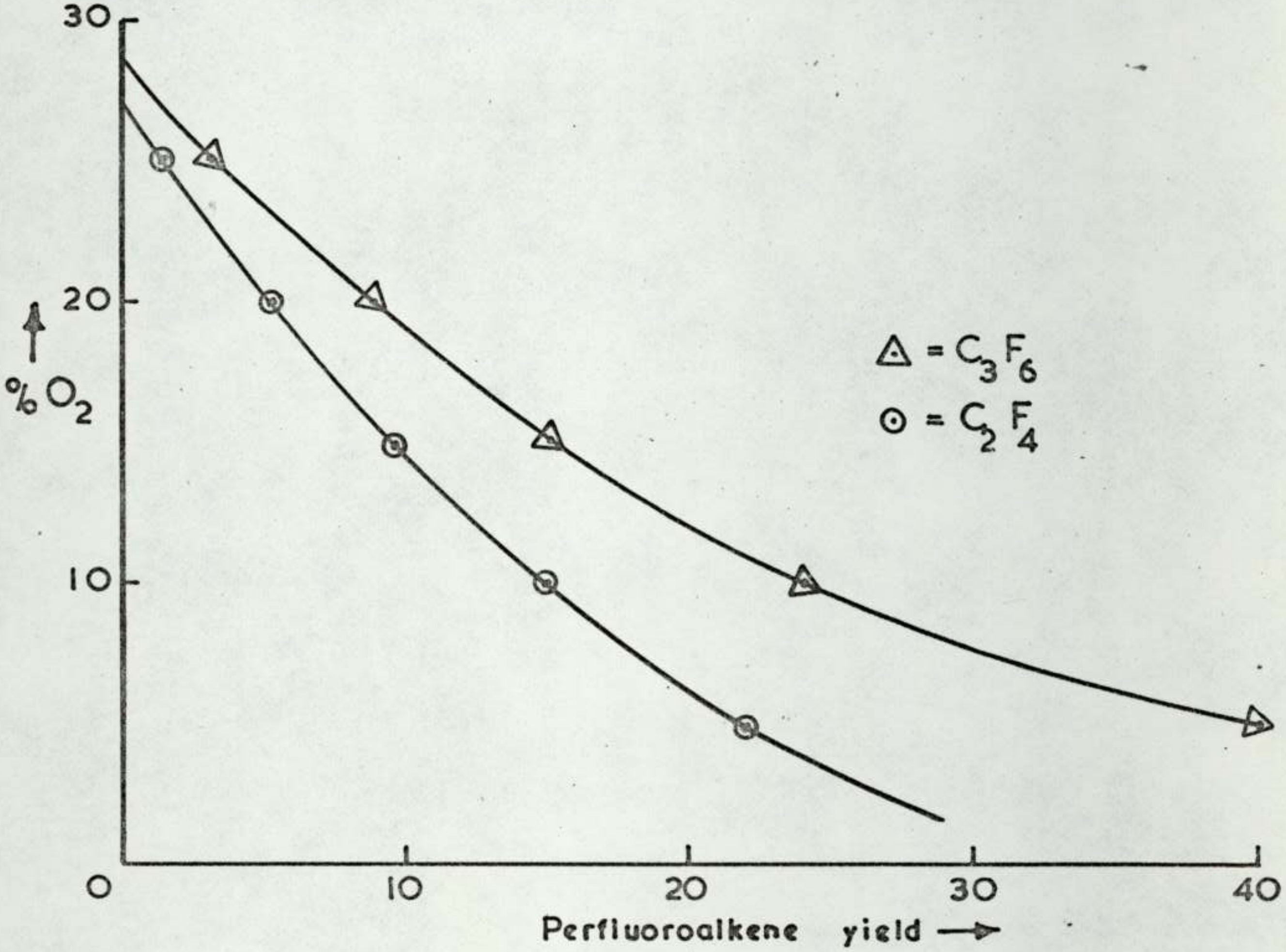
11.4.2 Oxygen

Oxygen was added to perfluorocarbon gases and vapours in various proportions and subjected to d.c. sparking or a.c. arcing. A reduction in yield of perfluoroalkene products was observed to be **regularly** dependant on oxygen concentrations. This is illustrated by figure 21 . It can be seen that relatively large concentrations of about 28% were necessary to eliminate perfluoroethylene and perfluoropropene. If the parent compound was itself a perfluoroalkene then its perfluoroalkene products were unaffected. This behaviour parallels that observed with nitric oxide and indicates that oxygen atoms liberated by the discharge attack the perfluoroalkenes or possibly their precursors. The following reactions are known to occur in suitable circumstances:



$$CF_3-CF=CF_2+O \rightarrow \left[CF_3-\underset{\diagdown O \diagup}{CF-CF_2} \right]^{\ddagger} \rightarrow CF_2=CF_2+CF_2O$$

$$CF_2=CF_2+O \rightarrow \left[\underset{\diagdown O \diagup}{CF_2-CF_2} \right]^{\ddagger} \rightarrow CF_2O+CF_2:$$



Reduction in yield of perfluoroalkenes from C_2F_6 with addition of oxygen

FIGURE 21

These reactions probably occur in the thermal discharge system and convert perfluoroalkenes to CF_2O. The presence of CF_2O was indicated by corrosion of the electrodes, the formation of hydrogen fluoride with water, and fuming in air. Concentrations of oxygen of about 40% caused explosive combustion of most perfluorocarbons.

As with nitric oxide, large concentrations of oxygen reduced the yields of 'soot'. About 10% of oxygen was sufficient completely to prevent 'soot' formation from perfluoropentane and perfluorohexane subjected to d.c. sparking. Wax-like polymer was also inhibited. Yields of saturated products were unaffected.

11.4.3 Hydrogen

Perfluorocarbon compounds subjected to d.c. sparking in the presence of hydrogen yielded some hydrogen fluoride. No mixed hydrofluorocarbon products were observed. This is to be expected since the formation of hydrogen fluoride is particularly favourable, having a bond energy of 135k cal mol^{-1} which enables hydrogen atoms liberated by the discharge to abstract fluorine atoms from perfluoroalkyl species.

11.4.4 Hydrofluorocarbon

It was of interest to observe the fate of combined hydrogen in the form of a hydrofluorocarbon. Undecafluorocyclohexane supplied by the Imperial Smelting Corporation was subjected to d.c. sparking in the vapour phase in helium carrier gas. No mixed hydrofluorocarbon products were detected and an amount of hydrogen fluoride was formed which corresponded approximately to the amount of undecafluorocyclohexane decomposed. This behaviour is consistent with the behaviour of hydrogen added to a perfluorocarbon described above, since similar considerations of energy apply.

By comparison with the product distribution obtained from perfluorocyclohexane, the undecafluorocyclohexane yielded more 'soot'-like and waxy polymer and less perfluoroalkene. The formation of a larger proportion of polymer corresponds with the effective conversion of undecafluorocyclohexane to perfluorocyclohexene by elimination of hydrogen fluoride.

11.4.5 Water

Perfluorocarbon compounds subjected to d.c. sparking in the presence of water in the liquid phase, or with water vapour in the gaseous or vapour phase, yielded hydrogen fluoride. No hydrofluorocarbon, hydroxy, or oxygen-containing fluorocarbons were detected. Perfluoroalkene yields were reduced. It is probable that hydrogen fluoride resulted from abstraction of fluorine atoms by liberated hydrogen atoms, and from hydrolysis of CF_2O produced by oxidation of perfluoroalkenes. Therefore the effect of water is, as might be expected, a combination of the effects of hydrogen and oxygen.

11.4.6 Nitrous oxide

Nitrous oxide is an efficient scavenger of thermal electrons and has been used as such in radiolytic systems:

$$N_2O + e \rightarrow \left[N_2O^-\right] \rightarrow N_2 + O^-$$

The measurement of yields of oxygen and nitrogen from this reaction has been suggested as a means of dosimetry (112). The oxygen ions can provide an alternative recombination reaction for positive ions and so give information concerning them. Thus the reduced yield of hydrogen in the presence of nitrous oxide from the radiolysis of hydrocarbon has been attributed to the replacement of the reaction

$$C_nH_{2n+2}^{+} + e \rightarrow C_nH_{2n} + H_2$$

by

$$C_nH_{2n+2}^{+} + O^- \rightarrow C_nH_{2n+2} + O$$

Although the perfluorocarbon analogue of the latter reaction would not be favourable, an alternative recombination would probably alter the product distribution if perfluorocarbon positive ions are important species in the degradation process. Nitrous oxide was therefore added to perfluorocarbons and subjected to thermal discharge. Product distributions were unaffected, which tends to support the view that ionic reactions are not of great importance in the discharge chemistry.

11.4.7 Two component perfluorocarbon mixtures

When a mixture of two perfluorocarbons is subjected to thermal discharge, the product distribution obtained is the additive combination of the product distributions given by each individual perfluorocarbon. Allowance must be made for the relative concentration and for the relative stability of the perfluorocarbons in the thermal discharge. Sacrificial and non-sacrificial protective effects as reported for some multicomponent systems subjected to radiolysis are not apparent, further indicating that the energy transfer processes that can occur in such systems are not important in the thermal discharge.

It can be seen from table 4 that unsaturated perfluorocarbons are more stable than saturated perfluorocarbons and that for the latter there is a decrease in stability with increase in molecular weight. This relative behaviour corresponds with hot filament pyrolysis studies (79).

11.5 Discussion of thermal discharge results

11.5.1 Basic degradation processes

The major products resulting from the thermal discharge activation of perfluorocarbons can be seen from table 3 to be perfluoroalkanes and perfluoroalkenes of carbon numbers one, two, and three. Perfluoroethylene is particularly important. Polymeric products are also major products from some cyclic and unsaturated perfluorocarbons. Products of carbon number intermediate between three and that of the parent compound are generally very minor, even when the parent compound has a carbon number as high as ten or eleven.

Partial degradation of large molecules appears to be unfavourable, indicating either a violent process involving the scission of several bonds simultaneously or a stepwise sequence of milder dissociations. At the pressures used, the localization of sufficient energy into a molecule to enable its violent dissociation into more than two fragments is improbable unless all molecules in the discharge are sufficiently highly activated to preclude stabilization by sharing energy with neighbours. However, the variation in stability of perfluorocarbon compounds in the thermal discharge indicates that only a proportion of molecules in the discharge received sufficient energy to decompose. The degradation of large molecules to give the products of carbon number one to three must therefore occur by a stepwise sequence of dissociations. The very small proportions of products of carbon number between that of the parent and three shows that the continuation of the sequence is remarkably efficient.

The nature of the products formed, particularly the perfluoroalkenes and the soot, are characteristic of pyrolysis which is the expected result of thermal discharge activation. Decomposition due to electronic excitation will be minimal and masked by the considerably greater degree of thermal decomposition. It can be seen that a thermal regime is compatible with the efficient stepwise conversion to products envisaged since the probability of thermal activation for all species in the discharge is high. In a non-thermal regime this would not be the case since the probability of activation will be low and the efficiency of stepwise conversion will decrease rapidly with the number of steps involved allowing stabilization of products of intermediate molecular weight.

Comparison of the liquid phase product distributions with those of the vapour phase indicates that the liquid phase is conducive to the formation of perfluoromethane, perfluoropropane and perfluoropropene at the expense of perfluoroethylene. It is possible that alternative scission processes of the parent molecule are favoured in a more condensed phase. It is more probable, however, that the thermal activation of the primary scission fragments, so producing further dissociation, is less favourable in the more condensed phase.

A comparison of the relative proportions of individual products from parent perfluorocarbons having a range of carbon-fluorine stoichiometry shows clearly that stoichiometry is not a strong influence on the yields of individual products, although the product distribution as a whole must reflect the stoichiometry of the parent compound. It could not be considered therefore that complete scission of the molecule into atoms, followed on quenching by recombination processes, could account for the product distributions obtained. Similarly, thermodynamic equilibration of products cannot occur to a significant extent because the variation of the proportions of individual species at a given temperature on the basis of a minimization of free energy will be regular with variation of the overall stoichiometry. This conclusion is not altered by any subsequent following of disequilibrium pathways that can be envisaged when the system is quenched to ambient temperatures and kinetic limitations affect recombination processes unequally. Thermodynamic equilibration of products has, however, been demonstrated in other thermal discharge systems under favourable conditions, for example in the plasma jet and the radio frequency induction plasma(66). In these systems, temperatures were typically 10000°K, and residence times were about one second. It is concluded that kinetic considerations restrict processes occurring in the spark and arc plasmas generated in the present work, and therefore temperatures and residence times are appreciably lower than those reported above.

The relative proportions of the various single carbon moieties CF_n that can be formed by the fission of all carbon-carbon bonds of the parent compound compared with the relative yields of products composed of these moieties shows that there is some relationship. Thus, it can be seen that CF_3 groups have some tendency to become converted to CF_4 and to C_2F_6, CF_2 groups to C_2F_4, and CF groups to polymer and to C_3F_6. This effect is limited by the extent to which fluorine atoms are redistributed in the scission process, or by subsequent reactions. A measure of the redistribution of fluorine atoms is readily obtained by a comparison of the proportion of CF_n groups in the parent molecule with the proportion in the product distribution. This analysis shows that for non-cyclic compounds in the gaseous and in the vapour phase, the fate of some CF_3 and CF is conversion to CF_2, but vice-versa in the liquid phase. CF_2 groups in cyclic compounds become converted to some extent to CF_3, CF, and C. The extent of such fluorine atom redistributions, which accompany thermal discharge degradation, is variable but involves on average, about 30% of fluorine atoms. A simple mechanistic interpretation of thermal discharge degradation in terms of scission of all carbon-carbon bonds of the parent molecule followed by recombination of the constituent CF_n groups is therefore precluded.

Furthermore, the individuality of product distributions, which, as described above, can only be rationalized in part by a consideration of single carbon atom moieties, implies that the degradation process is influenced by the structure of the parent molecule as a whole. Clearly a structural influence can only be exerted by a primary fragmentation process in which fragments containing several carbon atoms are formed. It is envisaged that dissociation of the parent molecule into two fragments is the primary process, which may be followed, depending upon the size of the fragments, by secondary activated dissociations of these fragments to result finally in fragments of carbon numbers one to three. Quenching of the plasma allows simple recombination of radicals. More extensive chemical reaction is precluded as this would lead to a loss of the individuality of product distributions that is observed.

11.5.2 'Soot' formation

The formation of soot from hydrocarbons in a flame has been studied extensively but is still not well understood in mechanistic terms. Evidence has been accumulating in recent years in favour of acetylene as the major initial precursor. Acetylenic radicals are believed to condense to form polyacetylenes which cyclize and cross-link to form the graphitic structure of soot. Some hydrogen remains to give a stoichiometry of typically C_8H.

Soot formation from perfluorocarbon compounds may occur in an analogous manner from fluoroacetylenic radicals formed in the discharge plasma. The retention of a comparatively larger proportion of fluorine atoms in the final structure is not surprising in view of the stability of the carbon-fluorine bond and hence the greater resistance to elimination of fluorine compared with hydrogen.

It has been shown recently that residence times and quenching rates can be important factors governing product formation in discharge-augmented flames (105). The operation of kinetic constraints is the most probable explanation of the difference observed in the ability of the d.c. spark and a.c. arc to generate soot. The very short duration of the high current spark, which is of the order of nanoseconds, may operate in favour of soot formation by kinetically restricting competitive reactions.

The observed reduction in the yield of soot in the presence of oxygen parallels the behaviour in hydrocarbon flame systems. Soot yields in such systems usually vary inversely with oxygen concentration and this has been attributed to the combustion of the soot and its precursors(107) (108).

11.5.3 Mechanistic schemes

The principle chemical effect of the thermal discharge is pyrolysis. Pyrolysis reactions normally proceed via the dissociation of vibrationally-excited molecules to free radical or molecular fragments. Free radical chain reactions are often important pyrolysis reactions. It has not been possible to establish whether free radical reactions are of major importance in the degradation of perfluorocarbons in the thermal discharge, probably because the inhomogeneity of the system largely prevented the action of scavengers. Nevertheless, it is possible that free radical processes are of some importance and it is worthwhile postulating molecular and radical mechanistic schemes. Such schemes may not of necessity be good representations of actual processes but can allow a rationalization of the product distributions observed.

The thermal activation of intermediate products is considered to be an important feature of the overall mechanism. The probability of such intermediate products undergoing activated dissociation will be related to their size and structure. Larger fragments will be more prone to undergo thermally activated dissociation than smaller ones. Perfluoroalkene products will be more resistant to further dissociation than perfluoroalkanes and perfluoroalkyl radicals. It is postulated that an important mode of formation of perfluoroalkenes from perfluoroalkanes in the thermal discharge is the thermally activated loss of fluorine from perfluoroalkyl radicals.

Some possible mechanistic schemes embodying these principles are given overleaf.

(i) Perfluoroethane

$$\begin{aligned}
\left[CF_3 - CF_3\right]^{\ddagger} &\rightarrow CF_3\cdot + CF_3\cdot && (1)\\
&\rightarrow C_2F_5\cdot + F\cdot && (2)\\
\left[C_2F_5\cdot\right]^{\ddagger} &\rightarrow C_2F_4 + F\cdot\\
C_2F_5\cdot + CF_3\cdot &\rightarrow C_3F_8\\
CF_3\cdot + F\cdot &\rightarrow CF_4
\end{aligned}$$

The observed results would require the initial processes (1) and (2) to have a similar probability.

(ii) Perfluoropropane

$$\begin{aligned}
\left[CF_3 - CF_2 - CF_3\right]^{\ddagger} &\rightarrow C_2F_5\cdot + CF_3\cdot && (1)\\
&\rightarrow C_3F_7\cdot + F\cdot && (2)\\
\left[C_2F_5\cdot\right]^{\ddagger} &\rightarrow C_2F_4 + F\cdot\\
\left[C_3F_7\cdot\right]^{\ddagger} &\rightarrow C_3F_6 + F\cdot\\
CF_3\cdot + CF_3\cdot &\rightarrow C_2F_6\\
C_2F_5\cdot + F\cdot &\rightarrow C_2F_6\\
CF_3\cdot + F\cdot &\rightarrow CF_4
\end{aligned}$$

The observed results would require reaction (1) to be the major initial dissociation.

(iii) Perfluoropropene

$$\left[CF_3 - CF = CF_2\right]^{\ddagger} \rightarrow C_2F_4 + CF_2: \qquad (1)$$

$$\rightarrow C_2F_3\cdot + CF_3\cdot \qquad (2)$$

$$n\left[C_2F_3\cdot\right]^{\ddagger} \rightarrow \left[C_2F\right]_n + 2nF\cdot$$

$$CF_2: + CF_2: \rightarrow C_2F_4$$

$$CF_3\cdot + CF_3\cdot \rightarrow C_2F_6$$

$$CF_3\cdot + F\cdot \rightarrow CF_4$$

The observed results would require reaction (1) to be the major initial dissociation.

(iv) Perfluorobutyne - 2

$$\left[CF_3 - C \equiv C - CF_3\right]^{\ddagger} \rightarrow C_3F_3\cdot + CF_3\cdot$$

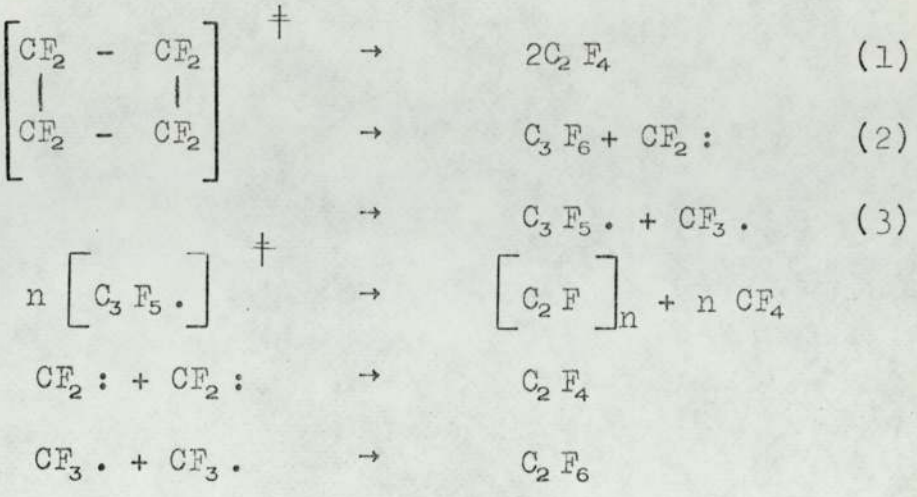
$$n\left[C_3F_3\cdot\right]^{\dagger} \rightarrow \left[C_2F\right]_n + nCF_2:$$

$$CF_2: + CF_2: \rightarrow C_2F_4$$

$$CF_3\cdot + CF_3\cdot \rightarrow C_2F_6$$

$$CF_3\cdot + F\cdot \rightarrow CF_4$$

(v) Perfluorocyclobutane



$$\left[\begin{array}{ccc} CF_2 & - & CF_2 \\ | & & | \\ CF_2 & - & CF_2 \end{array}\right]^{\ddagger} \rightarrow 2C_2F_4 \quad (1)$$

$$\rightarrow C_3F_6 + CF_2: \quad (2)$$

$$\rightarrow C_3F_5\cdot + CF_3\cdot \quad (3)$$

$$n\left[C_3F_5\cdot\right]^{\ddagger} \rightarrow \left[C_2F\right]_n + n\,CF_4$$

$$CF_2: + CF_2: \rightarrow C_2F_4$$

$$CF_3\cdot + CF_3\cdot \rightarrow C_2F_6$$

The observed results would require reaction (1) to be about ten times more probable than either (2) or (3).

Reactions (1) and (2) are the major decomposition modes observed in shock tube thermal decomposition studies (80) (81). Using the activation energies measured for these reactions in that work of 74 and 87k cal.mole $^{-1}$ respectively, and ignoring the minor reaction (3), the effective vibrational temperature of the perfluorocyclobutane in the discharge plasma can be calculated to be about 3000°K.

(vi) Perfluorobutene - 2

$$
\begin{aligned}
\left[CF_3\text{-}CF{=}CF\text{-}CF_3\right]^{\ddagger} &\rightarrow 2C_2F_4 && (1)\\
&\rightarrow C_3F_5\cdot + CF_3\cdot && (2)\\
&\rightarrow C_3F_6 + CF_2: && (3)\\
n\left[C_3F_5\cdot\right]^{\dagger} &\rightarrow \left[C_2F\right]_n + nCF_4\\
CF_3\cdot + CF_3\cdot &\rightarrow C_2F_6\\
CF_2: + CF_2: &\rightarrow C_2F_4
\end{aligned}
$$

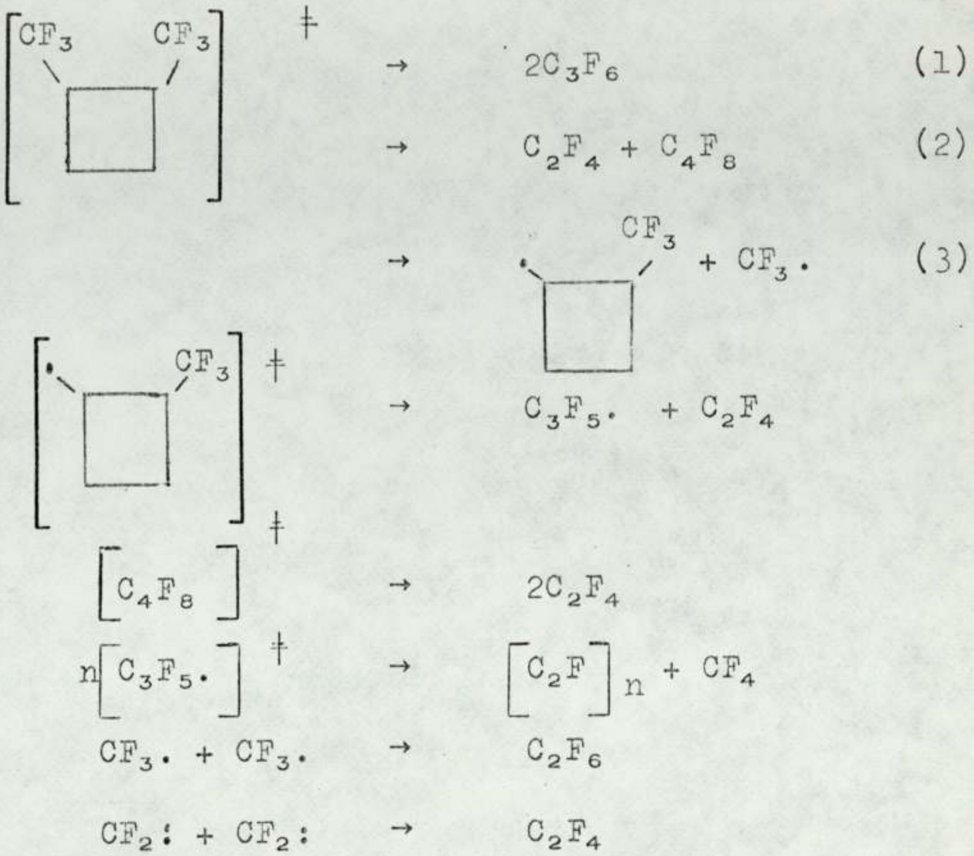
The observed results would require reaction (1) to be about twice as probable as either (2) or (3).

(vii) Perfluoropentane

$$
\begin{aligned}
\left[CF_3CF_2CF_2CF_2CF_3\right]^{\dagger} &\rightarrow C_3F_7\cdot + C_2F_5\cdot && (1)\\
&\rightarrow C_4F_9\cdot + CF_3\cdot && (2)\\
\left[C_2F_5\cdot\right]^{\ddagger} &\rightarrow C_2F_4 + F\cdot\\
\left[C_3F_7\cdot\right]^{\ddagger} &\rightarrow C_3F_6 + F\cdot\\
\left[C_4F_9\cdot\right]^{\ddagger} &\rightarrow C_4F_8 + F\cdot\\
\left[C_3F_6\right]^{\ddagger} &\rightarrow C_2F_4 + CF_2:\\
\left[C_4F_8\right]^{\ddagger} &\rightarrow C_3F_6 + CF_2:\\
&\rightarrow 2C_2F_4\\
CF_2: + CF_2: &\rightarrow C_2F_4\\
CF_3\cdot + F\cdot &\rightarrow CF_4\\
C_2F_5\cdot + F\cdot &\rightarrow C_2F_6\\
C_3F_7\cdot + F\cdot &\rightarrow C_3F_8\\
C_4F_9\cdot + F\cdot &\rightarrow C_4F_{10}
\end{aligned}
$$

Perfluorohexane and other perfluoroalkanes could degrade by a similar reaction sequence.

(viii) Perfluorodimethylcyclobutane



The product distributions obtained were markedly dependent upon the phase. In the vapour phase reactions (1) and (2) would, according to the above scheme, have a similar probability, and reaction (3) would have a relatively low probability. In the liquid phase reaction (1) becomes twice as probable as reaction (2), and reaction (3) has an increased, but still relatively low, probability.

12. NON-THERMAL DISCHARGE STUDIES

12.1 Apparatus

The apparatus used to generate the non-thermal discharge was of the Siemens ozonizer type. This is shown in figure 22 and consists of two concentric soda glass tubes of length 60cm, the inner of 2.5cm o.d. and the outer of 2.9cm i.d., thus giving a 2mm annular spacing. The electrodes are on the outer surface of the outer tube and the inner surface of the inner tube to avoid direct contact between the electrodes and a substrate passed through the annular spacing. The inner electrode consisted of a salt solution with a central conductor, and the outer electrode consisted of a sheet of aluminium foil tightly would around the outer tube. The electrodes were in contact with a 50cm length of the concentric tubes. Application of a 15kV 50 cycle a.c. power supply enabled a capacitative transfer of current between the electrodes generating a striated discharge throughout the annular spacing. About 1mA at 15kV was drawn by this system. Heating effects were minimal producing no more than a 10°C rise in wall temperature within the duration of an experiment. After using the apparatus with perfluoropropane, a thin hard film of polymeric material with the characteristics of PTFE had built up on the internal walls of the annular space. This was firmly attached and could be washed with solvents. As discussed previously, such a surface

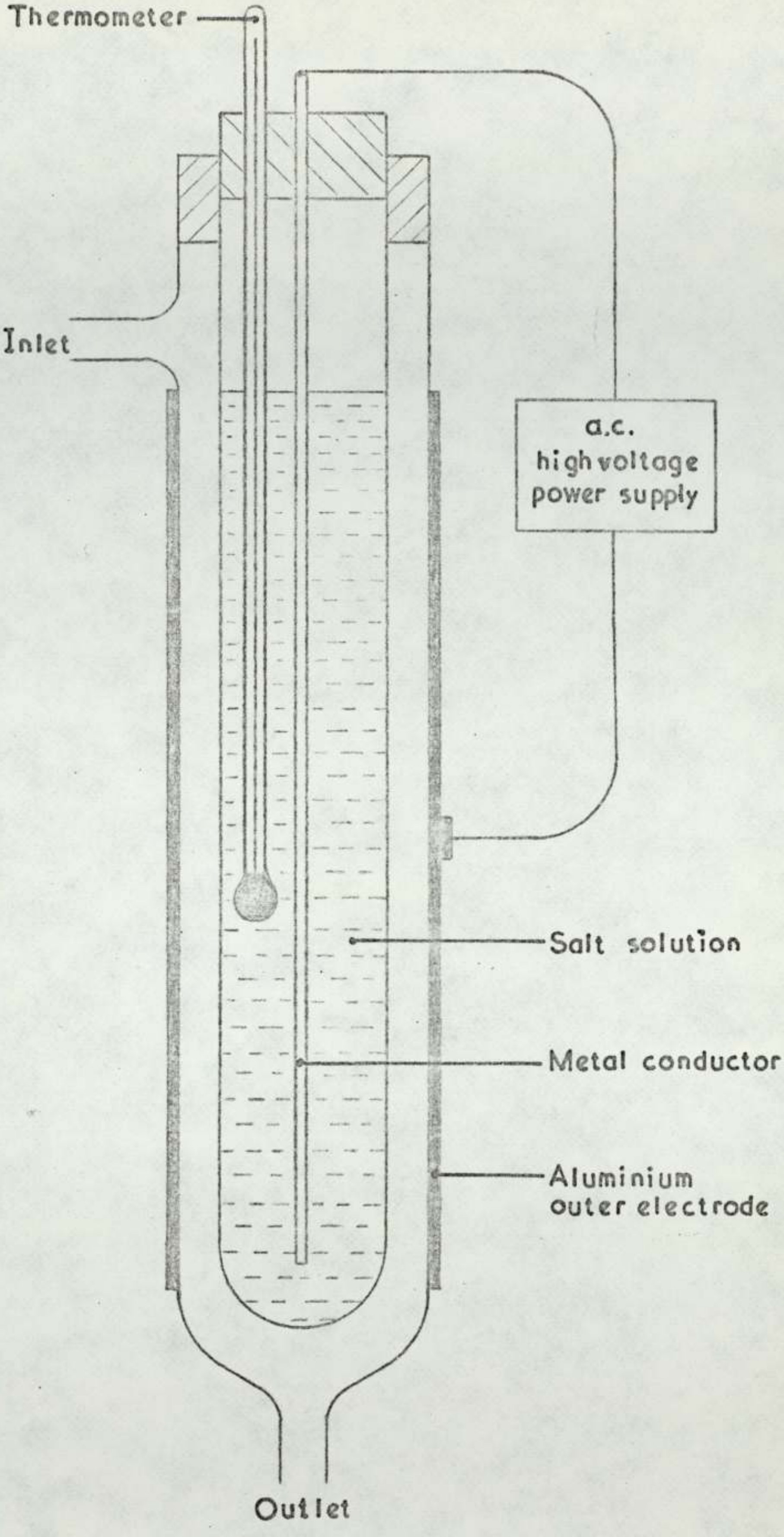


FIGURE 22

Non-thermal discharge apparatus

has the advantage of catalytic inactivity and will minimise the extent of wall reactions. The polymeric film was therefore allowed to remain.

12.2 Experimental procedure

Before each experiment the apparatus was thoroughly washed with solvents. The system was then flushed with inert gas until analysis of a sample by gas chromatography showed that perfluorocarbons from previous experiments and cleaning solvents were completely eliminated. The substrate gas or vapour was then passed through the apparatus at atmospheric pressure, via needle valves and flow meters, and the discharge was switched on. Vapours were supported by an inert carrier gas using a saturator as in the thermal discharge work described previously.

After allowing sufficient time for equilibrium to be achieved in the discharge zone, usually five to ten minutes, the exit gases were sampled by syringe and subjected to gas chromatographic analysis. The experiment was repeated under identical conditions until consistent results were obtained. The reproducibility of product distributions was generally good, although the degree of conversion to products was subject to some variation. It was evident that the degree of conversion to products was dependent on the current density but this factor was not amenable to complete control.

12.3 The effect of flow rate variation

Flow rates of the substrate gas through the apparatus of 7ml min^{-1} to 70ml min^{-1} were used. It was found that both the product distribution and the degree of conversion to products were almost independent of flow rate. This behaviour therefore contrasts with that observed with the thermal discharge where conversion to products was inversely proportional to flow rate. Clearly degradation in the non-thermal discharge must involve equilibrium between the parent compound and its products. This is not unexpected since reaction behaviour in apparatus of the Siemens ozonizer type has often been reported to be governed by considerations of equilibria(114). It follows from the insensitivity to flow rate that such equilibria are rapidly achieved. It is probable that the non-thermal discharge activates a proportion of the parent molecules, this proportion being governed by the current density, and the activated parent molecules are in equilibrium both with their products and with the non-activated parent molecules.

12.4 The effect of dilution of perfluorocarbon gases with inert gases

Perfluorocarbon gases were diluted with krypton and helium and subjected to the non-thermal discharge. Product distributions were found to be

Table 5 Part (i)

Product compositions obtained by non-thermal discharge

Parent Compound	C_2F_6	C_3F_8	C_3F_6	C_4F_8-2
Product	Molar percentages of total product yield			
CF_4	55	30	1.8	8.4
C_2F_4		0.12	42	5.4
C_2F_6		33	5.7	20
C_3F_6				12
C_3F_8	38		1.2	10
C_4F_8			18	
C_4F_{10}	3.7	11		
C_5F_{10}			5.7	
C_5F_{12}	2.3	6.1		9.8
C_6F_{12}			7.8	
C_6F_{14}	0.78	3.0		1.0
C_7F_{14}			1.0	
C_7F_{16}		1.0		0.5
C_8F_{18}				1.7
Polymer;		15	17	30
estimated as:		$[C_3F_6]_n$	$[C_3F_5]_n$	$[C_4F_6]_n$

Table 5 Part (ii)

Product compositions obtained by non-thermal discharge

Parent Compound	$n\text{-}C_4F_6$	$c\text{-}C_4F_6$	$n\text{-}C_5F_{12}$(v)	$n\text{-}C_6F_{14}$(v)
Product	Molar percentages of total product yield			
CF_4			13	16
C_2F_4		47	0.2	0.9
C_2F_6		0.6	20	26
C_3F_6		21	0.2	0.2
C_3F_8		0.5	20	18
C_4F_8		0.6		
C_4F_{10}			10	8.1
C_5F_{10}		1.1		
C_5F_{12}				3.8
C_6F_{12}		0.9		
C_6F_{14}		0.2	1.9	
C_7F_{14}		0.4		
C_7F_{16}			0.9	0.5
C_8F_{16}		0.2		
C_8F_{18}			0.4	0.4
Polymer:	100	28	25	26
estimated as:	$[C_4F_6]_n$	$[C_4F_4]_n$	$[C_5F_{10}]_n$	$[C_6F_{12}]_n$

Table 6

Relative stability towards non-thermal discharge

Compound	Stability*
CF_4	∞
C_2F_6	60
C_3F_8	20
C_3F_6	70
c-C_4F_8	100
C_4F_8-2-ene	45
c-C_4F_6	18
n-C_4F_6	35
C_5F_{12}	14
C_6F_{14}	12

*Relative to arbitary value of 100 for c-C_4F_8

unchanged by the presence of the inert gas. The degree of conversion to products was found to be directly proportional to the extent of dilution of the perfluorocarbon substrate. A dilution of about ten times doubled the degree of conversion to products. This effect could arise from various energy transfer processes. Inert gases have been observed to increase the radiolytic degradation of perfluoroethane by electronic excitation transfer. Such processes are strongly dependent on the excitation potentials of the donor and acceptor and are therefore specific in nature. Since in the present work both helium and krypton produced the same behaviour, excitation transfer of this type is improbable. If however initial excitation to super-excited states occurs, less specific excitation transfer depending upon inter-molecular coupling strength with neighbouring molecules may be important. The intermolecular coupling strength in such cases will strongly affect the ability of a highly excited molecule to share its excitation energy with neighbouring molecules rather than dissociate(86). This provides a possible explanation of the inert gas effect observed since the intermolecular coupling strength of the excited parent molecule with the inert gas atoms will be far lower than with the unexcited parent molecules.

12.5 Product distributions

The distributions of products formed by the non-thermal discharge degradation of various perfluorocarbon gases and vapours is given in table 5. Each product is expressed in terms of its molar percentage of the total product yield.

12.6 The relative stability of perfluorocarbons in the non-thermal discharge.

The stability of perfluorocarbons in the non-thermal discharge was found to be dependent on their structure and varied over a wide range. Approximate relative stability values are given in table 6. Perfluoroalkenes were generally more stable than perfluoroalkanes, although perfluorocyclobutane was particularly stable. Perfluoromethane, having no carbon-carbon bonds, was exceptionally stable.

The relative stability of the perfluorocarbons in the non-thermal discharge paralleled that in the thermal discharge, as can be seen by comparison with table 4. In view of the completely different product distributions obtained from most perfluorocarbons in the two discharge regimes, this similarity might be unexpected. The same structual factors appear to govern stability in the non-thermal discharge and in the thermal discharge despite the probability that non-thermal discharge degradation arises from electronic excitation whilst that in the thermal discharge arises from vibrational excitation. However, before dissociation of an electronically excited molecule can occur, energy must be transferred to vibrational levels. On average the relative amounts of vibrational energy required for dissociation will be comparable.

12.7 The effect of nitric oxide on product distributions

The addition of several per cent of nitric oxide to perfluorocarbon gases subjected to the non-thermal discharge inhibited polymer formation. It is probable therefore that polymer formation occurs by a free radical process. With perfluoroethane as the parent compound, perfluoropropane and perfluorobutane products were also inhibited by low concentrations of nitric oxide. The yields of non-polymeric products from other parent compounds were not affected however. The use of nitric oxide as a radical scavenger did not, therefore, clearly indicate the nature of the processes leading to formation of non-polymeric products.

12.8. The effect of oxygen on the product distributions

Small concentrations of oxygen of the order of 1% have a negligible effect on product distributions when added to perfluorocarbon gases subjected to non-thermal discharge. Large concentrations of the order of 10% reduced the yields of polymeric and unsaturated products. This behaviour parallels that in the thermal discharge, and gives little information concerning the mechanisms of product formation.

12.9 Discussion of non-thermal discharge results

12.9.1 Basic degradation processes

The product distributions obtained in the non-thermal discharge are quite different from those obtained in the thermal discharge. Thus perfluoroalkane parent compounds yield largely polymeric and saturated products in the non-thermal discharge, in contrast to the high proportion of unsaturated products and very low proportion of polymeric products that they form in the thermal discharge. Furthermore, in the non-thermal discharge soot-like products are not formed; the major products cover a wider range of molecular weight relative to the parent compound than in the thermal discharge. The formation of a larger proportion of products of high molecular weight than the parent compound suggests that radical reactions of the primary fragments maybe more extensive in the non-thermal discharge.

A comparison of the proportion of CF_2 and CF_3 groups in the parent compounds with that of the products reveals almost no redistribution of fluorine atoms. It was deduced from the thermal discharge results than on average about 30% of the fluorine atoms were redistributed between the carbon atoms.

These factors demonstrate that the non-thermal discharge is a milder degradative regime than the thermal discharge and consequently may have a less complex chemistry.

The major activating process in the non-thermal discharge will be electronic excitation, hence the non-thermal discharge has been used as a means of generation of electronically-excited species, e.g. cyclohexane(110). Dissociation processes resulting from electronic excitation may be similar or dissimilar to those resulting from direct vibrational excitation, depending upon the effect that the changed electron distribution has on bond energies. The major features of the difference in product distributions in the two discharge regimes are considered to arise not from such possible differences in the initial dissociation reactions, but from the occurrence of secondary activated dissociations of the fragments which can take place in the thermal discharge but not in the non-thermal discharge. In a thermal discharge all species have a high probability of thermal activation whereas in the non-thermal discharge the probability of activation is low. The possibility of successive activation of the parent molecule and then its fragments is therefore limited in the non-thermal discharge. The virtual absence of perfluoroalkene products from perfluoroalkane parents in the non-thermal discharge and the lack of redistribution of fluorine atoms can be accounted for by the stability of perfluoroalkyl radicals in the non-thermal environment. It is postulated that in the thermal discharge, thermally activated perfluoroalkyl radicals will dissociate to a perfluoroalkene and a fluorine atom. In the thermal discharge the perfluoroalkyl radicals will recombine to form perfluoroalkanes of higher and lower molecular weight than the parent and will initiate polymerization processes. Polymerization to soot-like products occurs only in the thermal discharge however, and must therefore require activation of intermediate compounds.

It is of interest to compare the product distributions obtained from a hydrocarbon radical system, as generated for example by the γ-radiolysis of n-hexane(69), or the non-thermal discharge degradation of n-hexane(111), with those obtained from a perfluorocarbon system.

About 50% of the n-hexane consumed in the γ-radiolysis of n-hexane is converted to dimeric products and a further 20% is converted to hexenes. Hydrogen is also an important product(69). This is therefore in complete contrast to the product distribution obtained from perfluorohexane in the non-thermal discharge. The absence of analogy between the two systems is explicable in terms of the significantly different considerations of energy that apply. In particular, the strength of the C-F bond is about 20k cal mole^{-1} greater than that of the C-H bond. Since, on dissociation of the parent, scission of C-C bonds competes with scission of C-H or C-F bonds, C-C scission will be more dominant for perfluorocarbons.

The formation of dimer in hydrocarbon systems is known to occur by recombination of $C_nH_{2n+1}\cdot$ radicals, where the parent is C_nH_{2n+2}. As C-F bond scission is less favourable than C-H bond scission, the direct formation of $C_nF_{2n+1}\cdot$ is also less favourable. More significantly the reaction

$$C_nH_{2n+2} + H\cdot \rightarrow C_nH_{2n+1}\cdot + H_2$$

is probably the most favourable reaction for atomic hydrogen. The perfluorocarbon analogue is, however, precluded by the low binding energy of molecular fluorine and the high C-F bond energy. Furthermore, in the hydrocarbon system atomic hydrogen can react with the important product C_nH_{2n} :

$$C_nH_{2n} + H\cdot \rightarrow C_nH_{2n+1}\cdot$$

The formation of a large proportion of dimeric products from hydrocarbons, but not from perfluorocarbons, can thus be readily understood.

In hydrocarbons systems, an important process is the formation of alkenes corresponding to the parent hydrocarbon, and is believed to occur by the elimination of molecular hydrogen. The analogous elimination of fluorine is clearly not favourable. Alkenes can also be formed in hydrocarbon systems by the disproportionation of alkyl radicals. Photochemical studies have indicated that corresponding disproportionations between perfluoroalkyl radicals are unfavourable (87)(88).

Thus the formation of alkenes from alkanes in hydrocarbon systems but not in perfluorocarbon systems can be rationalized.

The non-thermal degradation of perfluoroalkanes is therefore simpler in many respects than the analogous hydrocarbon degradation system. Perfluoroalkanes are likely to undergo only two initial scission processes :

$$C_nF_{2n+2} \rightarrow C_nF_{2n+1}\cdot + F\cdot \qquad (i)$$

$$C_nF_{2n+2} \rightarrow C_mF_{2m+1}\cdot + C_{(n-m)}F_{2(n-m)+1}\cdot \qquad (ii)$$

process (i) having a lower probability than process(ii). The observed products should be interpretable in terms of simple recombination reactions of these radicals, together with polymer formation. Polymerization can occur by means of the reaction

$$C_mF_{2m+1}\cdot + C_nF_{2n+2} \rightarrow C_{m+n}F_{2(m+n)+1}\cdot \text{ etc.} + 2F\cdot \text{ (?)}$$

followed by termination by fluorine or perfluoroalkyl radicals. The fate of a perfluoroalkyl radical can therefore be recombination with a fluorine atom or perfluoroalkyl radical, or reaction with a molecule of the parent compound. The product distributions indicate that the probability of recombination decreases rapidly with increase in carbon number; recombination is relatively improbable beyond C_3F_7. Mobility considerations are probably of dominant importance.

The extent of conversion to polymer is related to the molecular weight of the parent compound since larger parent molecules will form larger perfluoroalkyl fragments on dissociation.

The degradation of perfluoroalkenes in the non-thermal discharge is more complex involving the formation of perfluoroalkanes, perfluoroalkenes, and polymeric products. Perfluoroalkane products were of lesser importance than perfluoroalkene products, but were more favoured in the non-thermal discharge than in the thermal discharge. Polymeric products containing some unsaturation were important, and for perfluorobutyne-2 were the sole products. Soot-like polymer was not formed, however. This contrasts with the thermal discharge which favours soot-like polymer.

The basic modes of product formation from perfluoroalkenes in the non-thermal discharge are probably similar to those advanced for perfluoroalkanes. Scission of the excited parent molecule into two fragments occurs in which C-C scission is favoured with respect to C-F scission. The radical fragments then compete for recombination, and for polymer formation by reaction with parent molecules. Molecular, non-radical products may also be formed directly by scission of the parent molecule. Activated dissociation of the initial fragments as postulated in the thermal discharge is not expected to occur in the non-thermal discharge.

13. SUMMARY OF DISCHARGE CONCLUSIONS

A range of aliphatic, alicyclic, and unsaturated perfluorocarbons has been subjected to thermal and non-thermal discharge. The product compositions were quite different in the two regimes. Analysis of the product compositions in terms of the structures of the parent compounds indicated the nature of the scission and product formation processes.

Thermal discharge degradation of perfluorocarbons was interpreted in terms of the vibrationally activated dissociation of the parent compound and, successively, its larger fragments. The products formed were mainly of low molecular weight containing one to three carbon atoms, of which perfluoroethylene was particularly important. Thermal activation enabled the formation of soot-like polymer from unsaturated parent compounds. Product distributions were governed by the structure of the parent compound but were not in simple relation to it. Thermodynamic equilibration of products did not occur; kinetic considerations were dominant. Product formation was attributed mainly to radical recombination. Direct formation of products could also occur as a direct consequence of the primary scission process.

Non-thermal discharge product distributions were indicative of a more simple mechanistic scheme. Dissociations of the parent compounds into two fragments by scission of a carbon-carbon bond, or with lower probability a carbon-fluorine bond, was attributed to electronic excitation. The radicals so formed then compete for recombination and for polymerization with parent molecules to give the observed product distribution. Direct formation of products by the primary scission process may also occur. The formation of perfluoro-alkane and polymeric products is favoured. Soot-like polymer is not formed. The activation of intermediate species to produce secondary dissociation is considered to be improbable in the non-thermal discharge and is the major difference between degradation in the two regimes.

Hydrocarbons are reported to yield hydrogen and dimers as major products of non-thermal discharge degradation. However it is shown that considerations of energy preclude the analogous formation of fluorine and dimer from perfluorocarbons.

The results in tables 3 and 5 show the product distributions which are to be expected when pure perfluorocarbons are used as insulator-coolants in electrical equipment and are subjected to severe electrical stress. It is demonstrated that hydrocarbons, hydrogen, water, and oxygen, should be absent from the system since otherwise the corrosive products CF_2O and/or HF will be formed.

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