THESIS

' A STUDY OF PHOSPHORUS PENTAHALIDES '

This Thesis is presented to the
University of Glasgow for the
Degree of Doctor of Philosophy.

by

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FOREWORD

The atoms of the Group V elements have outer electronic shells $(ns)^2$, $(np)^3$, each element forming a number of covalent compounds in which the bonds involve only hybridised s and p orbitals. In completing the s and p orbitals the Group V atom may be attached to three univalent groups such as $PHal_3$ or less commonly, four univalent groups such as $[PCl_4^+]$.

The phosphorus atom has also five 3d orbitals which although less stable than the 3s and 3p orbitals, are also available for bond formation. Craig et al have discussed the effect of bonding atoms on the ability of such an atom as phosphorus, to utilise d orbitals for bond formation (1). From this study, it appears likely that in order to form units of the type PX_5 or PX_6, the ligand group must possess a high electronegativity. This is certainly true in the halides of phosphorus since only chlorine and fluorine give molecules of this type; neither molecular PI_5 nor PBr_5 exist and the anion $[PBr_6^-]$ exists only in a solvent (acetonitrile) (2).

In keeping with the idea that hexa-substituted units would be expected to occur with only the most electronegative ligand, the hexafluorophosphate ion, $[PF_6^-]$, is well known in a number of compounds whereas the hexachlorophosphate ion, $[PCl_6^-]$, is known only in one case, solid phosphorus pentachloride, where it exists along with the tetrachlorophosphonium ion, $[PCl_4^+]$ (3).

It is of interest to consider, in more detail, the mixed pentahalides of phosphorus in the light of the "electronegativity effect" postulated by Craig and his co-workers.

Studies of the interaction of phosphorus trichloride and bromine have been numerous but there has been no substantial evidence to suggest the formation of bonds of the type discussed above (4 - 12).

However, in the chlorine-fluorine pentahalide system, one might predict that the formation of compounds of the type PX_5 and PX_6 would be more probable as a result of the highly electronegative nature of the ligand atoms.

The first member of this series, PF_3Cl_2, was prepared by Moissan in 1888, (13); up to the commencement of this work, however, little was known of its properties beyond that described in the original publications. A report of the re-investigation of the properties of PF_3Cl_2 is given in the first part of this thesis.

More recently, Booth and his co-workers have prepared PCl_2F and $PClF_2$ which on reaction with chlorine give products of the PX_5 type (14); no detailed examination of these reactions has been carried out.

While the work for this thesis was in progress, Kolditz published a series of papers on chlorine-fluorine pentahalides, which involved the preparation of the solid compounds, $[PCl_4^+][PF_6^-]$ and $[PCl_4^+]F^-$ (15) (16).

The existence of the ionic analogue of PF_3Cl_2 raises many interesting points concerning the reaction of these two types of compound, and also the possibility of interconversion of the two forms. Only a few of the aspects have been investigated so far; for the most part work has been concerned with the action of heat on these compounds, the pyrolysis of PF_3Cl_2 being referred to in Part I, that of $[PCl_4^+][PF_6^-]$ in Part II of this thesis.

It will be apparent from what follows that the conclusions reached by Kolditz are not always in agreement with those which emerge from the present studies.

In connection with the study of the fluorine-chlorine pentahalide system, detailed information of the thermodynamic properties of phosphorus pentachloride was required. Phosphorus pentachloride, which might almost be termed "the father of phosphorus halides" has been very extensively investigated. Indeed most elementary text-books contain references to the dissociation of phosphorus pentachloride into phosphorus trichloride and chlorine. However, examination of the literature shows that the thermodynamic data, particularly the equilibrium pressure (vapour pressure) and the vapour phase dissociation equilibrium of the compound is limited in certain aspects, especially with regard to the temperature range over which the investigation was carried out.

Thus, the equilibrium dissociation pressure of the solid, and the equilibrium constants of the dissociation of the phosphorus pentachloride molecule in the gas phase have been investigated more fully. A report on this study comprises the third part of this thesis.

NOMENCLATURE NOTE.

The Chemical Society has recommended the naming of phosphorus V compounds as derivatives of the hypothetical compound phosphorane, PH_5 e.g. the compound PF_3Cl_2 would be named dichlorotrifluoro:phosphorane. In the naming of ionic compounds of the type $[PX_4^+][PX_6^-]$, no recommendations have been made. The method commonly used for naming this type of compound can be illustrated for the solid $[PCl_4^+][PCl_5F^-]$ which would be tetrachlorophosphonium pentachloromonofluorophosphate. As these names are rather awkward, the following method has been adopted in this thesis: the common names phosphorus pentachloride, pentabromide and pentafluoride are retained; those compounds which are members of the mixed pentahalide series are written as formulae, thus: $[PCl_4^+][PF_6^-]$, $[PCl_4^+][PCl_5F^-]$, $[PCl_4^+]F^-$, $[PCl_4^+][PCl_5Br^-]$ and PF_3Cl_2.

PART I

A STUDY OF PF_3Cl_2.

INTRODUCTION.

Although mixed chloro-fluoro pentahalides of phosphorus had been known to exist towards the end of the nineteenth century, it is only recently that a detailed investigation of these compounds has begun.

The preparation of PF_3Cl_2 was first reported by Moissan in 1888, (13) and subsequently improved by Poulenc in 1891 (17). Moissan described this compound as a colourless non-inflammable gas formed by direct combination of phosphorus trifluoride with chlorine. The vapour density was reported as 5·39 - 5·42 (theor. 5·46) and the gas liquified at -8° under normal pressure. Moissan reported a disproportionation reaction which occurred according to the equation:

$$5PF_3Cl_2 \longrightarrow 2PCl_5 + 3PF_5.$$

either by heating to 200 - 250° or by the passage of an electric discharge. Controlled hydrolysis was reported to give phosphorus oxyfluoride and hydrogen chloride whilst complete hydrolysis yielded phosphoric acid, hydrogen fluoride and hydrogen chloride.

A number of the chemical reactions of PF_3Cl_2 were also mentioned by Moissan. Reaction with sulphur gave sulphur monochloride and thiophosphoryl fluoride whilst the metals mercury, magnesium, aluminium, tin, lead, iron, and nickel were attacked at 180° giving metal chlorides and phosphorus trifluoride. With absolute alcohol ethyl chloride, ethyl fluoride and some "phosphorous" acid were formed.

Since the investigation carried out by Moissan, PF_3Cl_2 has remained almost completely neglected.

Electron diffraction studies of PF_3Cl_2 by Brockway and Beach (18), showed the P-F bond distance to be 1·59Å and the P-Cl bond distance to be 2·05Å. The PF_3Cl_2 molecule was found to have the trigonal bipyramidal configuration in the vapour phase, with the two chlorine atoms at the apices of the two pyramids and the three fluorine atoms at the corners of their common base.

In 1957, the kinetics of the addition reaction of chlorine to phosphorus trifluoride were briefly reported by Wilson (19). In a pyrex vessel, the reaction at 0°, which was found to be heterogeneous, went to completion within 1%; the rate of reaction was approximately halved by raising the temperature from 0° to 25°. At 25° the rate of reaction in a paraffin coated vessel was less than one-tenth as great as that in a similar uncoated vessel; furthermore, the gas phase reaction was found to be photo sensitive. The reaction in the liquid phase at temperatures below the boiling-point of the mixture was many fold more rapid than in the gas-phase at 0°. Attack by the liquefied product of reaction, on the glass apparatus was found to be rapid at room temperature. This observation is in marked contrast to the results of this present work.

In a theoretical study, Jaffe (20) has discussed the possible incidence of π bonding in PF_3Cl_2. Generally penta-co-ordinated compounds of phosphorus form exclusively single bonds. However, due to the highly electronegative fluorine ligands in PF_3Cl_2, sufficient charge is inductively withdrawn from the phosphorus atom to give it a formal positive charge.

This leads to a non vanishing value of the overlap integral and thus some degree of π bonding.

Booth and his co-workers in the course of preparation of a series of fluorine containing trihalides, have observed their reaction with free halogen. No detailed investigation was carried out on the products of reaction although undoubtedly various chloro-fluoro pentahalides were obtained (14).

By controlled fluorination of phosphorus pentachloride with arsenic trifluoride, carried out in arsenic trichloride solution, Kolditz (15) obtained the compound $[PCl_4^+][PF_6^-]$ of identical composition to PF_3Cl_2 but differing from it in being clearly ionic in nature. The ionic structure of this compound was confirmed by conductance measurements in acetonitrile, a value of 140ohm.$^{-1}$cm.^{2} mole.$^{-1}$ being obtained for the molar conductivity (This report is further commented on later in the text). The sublimation temperature of $[PCl_4^+][PF_6^-]$ was reported to be 135°. Kolditz also reported the reaction between phosphorus pentafluoride and $[PCl_4^+]F^-$ at 135° as leading to formation of $[PCl_4^+][PF_6^-]$ together with PF_3Cl_2 (16). The possible isomerisation of the molecular to the ionic form has also been discussed by Kolditz who concluded that it was unlikely to occur (21). Thermal decomposition of $[PCl_4^+][PF_6^-]$ in arsenic trichloride is reported to lead to formation of phosphorus pentafluoride, $[PCl_4^+]F^-$ and PF_3Cl_2 (16). The molecular weight of solid $[PCl_4^+]F^-$ was determined cryoscopically in anhydrous acetic acid and a value of 80 (theor. M/2 = 96) given at a concentration of 0·05M; the displacement method of Victor Meyer gave a value of half the molecular weight of PCl_4F at 190°. The conductance of $[PCl_4^+]F^-$ in acetonitrile was taken as proof of the ionic nature of the solid compound, a value of 40 $ohm.^{-1}$ $mole.^{-1}cm^2$ being obtained at 21°. A liquid form of "PCl_4F" with a boiling point of 67° and a freezing point of -63° which had a specific conductance of $1{\cdot}6 \times 10^{-7}$ $ohm.^{-1}$ cm^{-1} at 190° (19°?) was prepared by fusing $[PCl_4^+]F^-$ at 177°.

EXPERIMENTAL RESULTS.

THE PREPARATION AND ANALYSIS OF PF_3Cl_2.

PF_3Cl_2 was prepared by mixing approximately equal volumes of phosphorus trifluoride and chlorine; the reaction was observed to take place in either the liquid or gaseous phase. The reaction was slow in the vapour phase but very rapid in the liquid phase. These observations are in keeping with those of Wilson quoted earlier. For preparative purposes, reaction was carried out in the liquid phase. The rate of reaction in the gas phase was found to be unaffected by irradiation by U.V. radiation, an observation which is in disagreement with Wilson's findings.

Care was taken to have a slight excess (e.g. 5%) of phosphorus trifluoride in the final reaction mixture, since this could be removed more easily than excess of chlorine.

In every preparation yields were below theoretical and varying amounts of a white solid were obtained. An X-ray powder photograph of this solid material showed it to be a mixture of $[PCl_4^+][PF_6^-]$ and $[PCl_4^+]F^-$. On storage the white solid sometimes volatilised and on occasions reformed as distinct crystals on the walls of the apparatus. A more detailed consideration will be given to the formation of this mixed solid material in the section concerned with the stability of PF_3Cl_2.

Separation of PF_3Cl_2 from the excess of phosphorus trifluoride always present and from traces of phosphorus oxyfluoride and silicon tetrafluoride was accomplished by repeated fractionation at low temperatures in a vacuum line employing vacuum taps lubricated with Fluorube "W" grease.

In the initial stages of the work, the purification was followed by vapour pressure checks; later, however, the I.R. spectra of gas samples were used for this purpose.

It was found that purified samples of PF_3Cl_2 could not be stored for any length of time without the formation of the white solid material mentioned above. Consequently, immediately before use, initially pure samples of PF_3Cl_2 had to be repurified by fractionation in vacuo.

It was found, however, that storage under liquid oxygen was an effective means of lengthening the lifetime of a pure sample of PF_3Cl_2.

A known amount of pure PF_3Cl_2 was hydrolysed by an excess of 0·1N sodium hydroxide and the resulting solution was analysed for phosphorus (volumetrically), chlorine (gravimetrically) and fluorine (by difference). The analytical results were as follows:

Found:	P, 19·4, 19·3,	Cl, 44·2, 43·9,	F, 36·4, 36·8%
Calculated:	P, 19·5	Cl, 44·6	F, 35·9 %

Determination of the vapour density of purified samples gave a value for the molecular weight of 159 ± 1 at 20° (required for PF_3Cl_2 : 158·9).

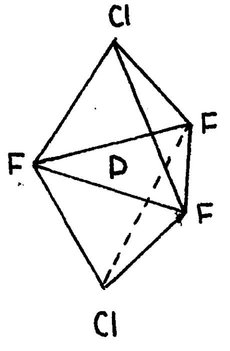
THE I.R. SPECTRUM OF PF_3Cl_2 VAPOUR.

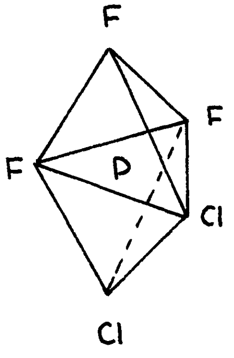
The details of the spectrum of PF_3Cl_2 vapour obtained at 5 mm. pressure were as follows:

930s, 920s, 904s,
899s, 870s, 675s,
668s, 635s, 564m,
492m, 432w. $cm.^{-1}$

At 40 mm. and 80 mm. pressure, additional peaks at 415m, and 530s, were obtained. The spectrum is reproduced in figure 1.

No attempt has been made to correlate these frequencies with the trigonal bipyramidal model of the molecule. Although it can be accepted as a general criterion, that symmetrical molecules have fairly simple spectra, these may be complicated by the existence of stereo-isomers. Thus, for PF_3Cl_2 the following configurations are possible:





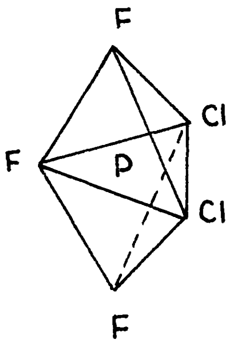
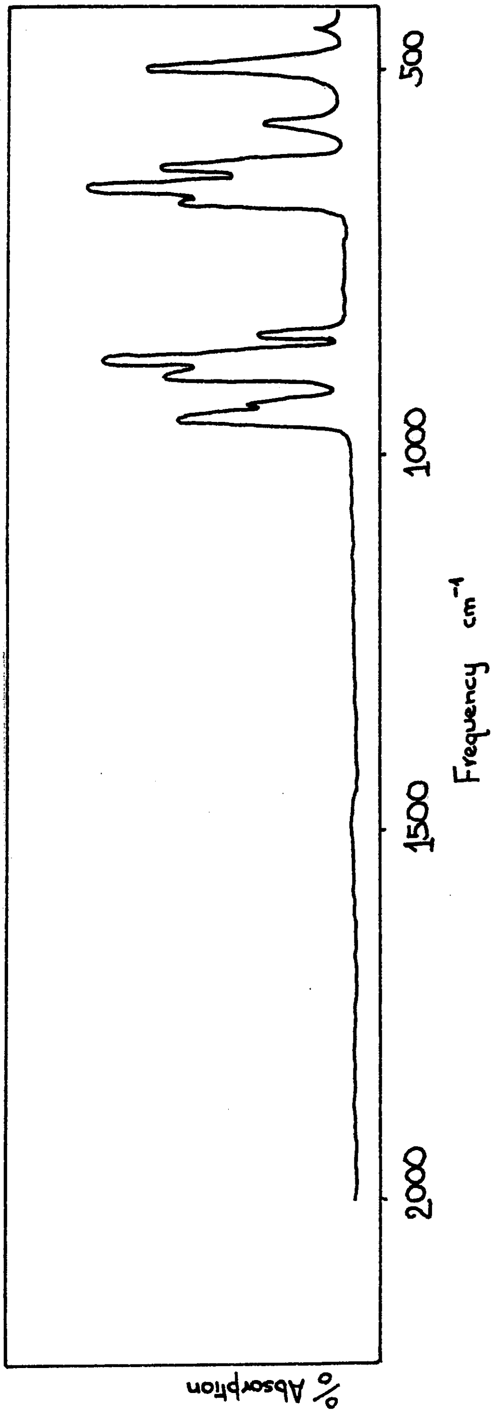


Fig. 1. The I.R. Spectrum of PF_3Cl_2.



From the detailed spectrum, it is seen that four frequencies are found in the P-F region; a symmetrical bipyramidal molecule would require only one. It is not possible, however, to draw any conclusions from these observations as it is very difficult to consider only isolated P-F vibrations; these bonds will almost certainly be influenced by the P-Cl vibrations in the molecule. It seems unlikely that stereo-isomeric forms exist since the results of the electron diffraction studies of Brockway and Beach are in keeping with the symmetrical configuration.

THE VAPOUR PRESSURE, BOILING POINT AND MELTING POINT OF PF_3Cl_2.

The pressures of three discrete samples of pure liquid PF_3Cl_2 were measured over a range of temperature by a static method employing a spiral gauge. The results are recorded in table 1. The temperature range studied was -10° to -60°, pressure readings being recorded for both ascending and descending temperatures. The results are shown graphically in figure 2, from which can be seen the linear relationship between the logarithim of the vapour pressure and reciprocal absolute temperature.

The vapour pressure equation was calculated by the method of least squares and was found to be:

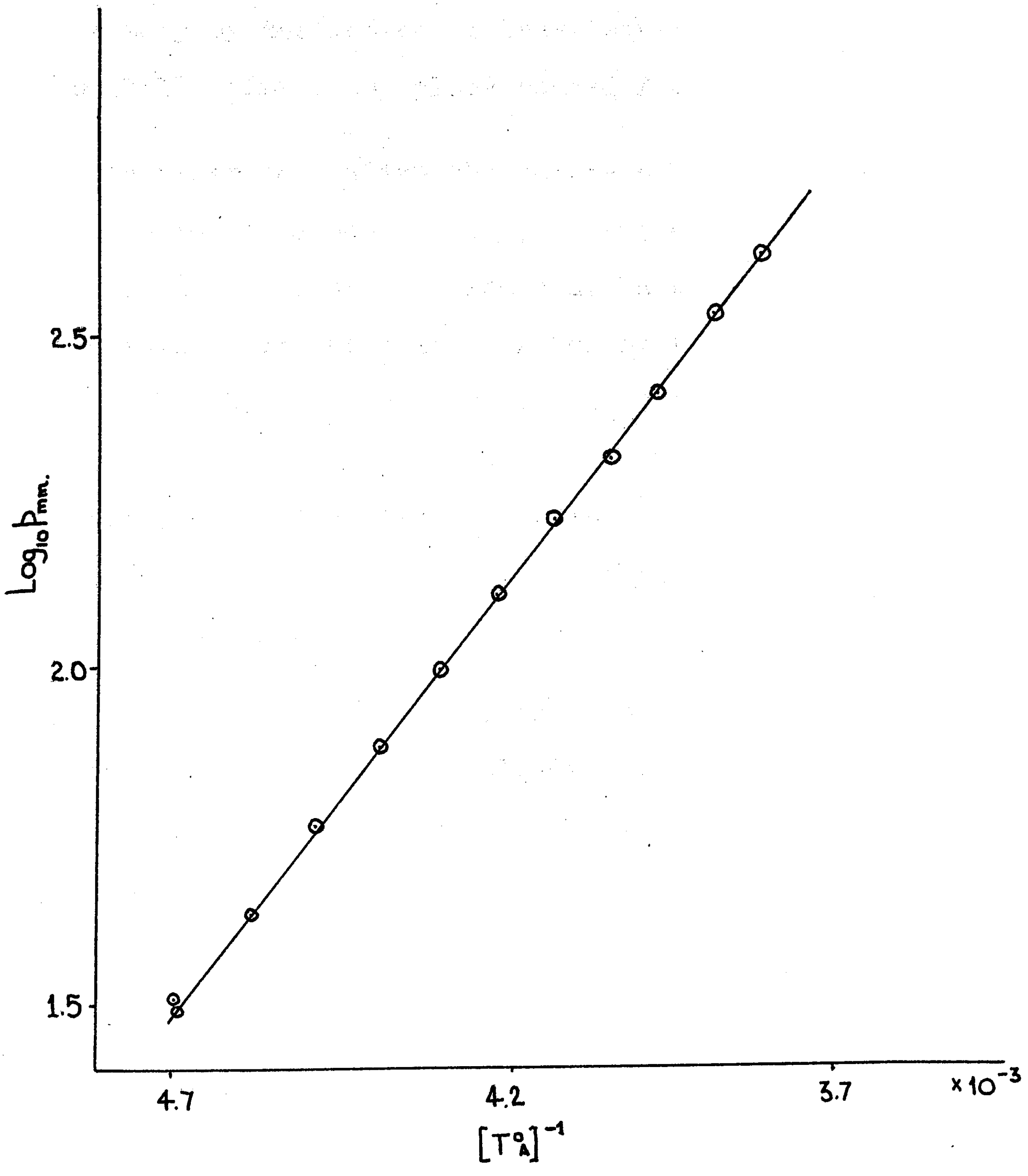
$$\mathrm{Log}_{10}p_{mm} = -1228T^{-1} + 7{\cdot}264.$$

This gave H for vapourisation to be 5•66K.cal. and a value of 20•2 for Trouton's Constant.

Table 1. Vapour Pressure of PF_3Cl_2.

Expt.	Temp °C	Press mm	$Log_{10}p_{mm}$	$Log_{10}p_{mm}$ calcd.	Δ $Log_{10}p_{mm}$
111A	-10	416·33	2·619	2·595	+0·024
111A	-15	336·84	2·527	2·514	+0·013
11A	-20	257·25	2·410	2·410	0·000
11A	-25	204·69	2·311	2·313	-0·002
11A	-30	161·68	2·209	2·211	-0·002
11D	-35	121·82	2·086	2·105	-0·019
111A	-40	96·70	1·985	1·993	-0·008
11D	-40	97·70	1·990	1·993	-0·003
111D	-45	68·39	1·835	1·877	-0·042
1D	-45	73·76	1·868	1·877	-0·009
1D	-50	58·35	1·766	1·757	+0·009
1D	-50	57·39	1·758	1·757	+0·001
11D	-50	58·90	1·771	1·757	+0·014
111D	-50	58·79	1·769	1·757	+0·012
11D	-55	44·19	1·645	1·631	+0·014
11D	-60	31·00	1·491	1·498	-0·007
1D	-60	32·10	1·507	1·498	+0·009

Fig. 2. The Vapour Pressure of PF_3Cl_2.



This latter value shows that in the liquid phase PF_3Cl_2 is not associated to any appreciable extent, although it is perhaps significantly different from the value usually attributed to normal liquids i.e. 22. By extrapolation, the boiling point determined accurately by the method of least squares, was shown to be 7·1°. (Previous values ranged from -8° to +10°).

In order to confirm the nature of the vapour in the vapour-liquid equilibrium, a sample was pumped off and its vapour density determined. A value of 160·1 was obtained for the molecular weight (theor. for PF_3Cl_2 158·9), and the vapour pressure of the system at -50° before and after this determination was 58·35 and 57·39 mm. respectively. Further the I.R. spectrum of this vapour sample showed only frequencies attributable to PF_3Cl_2.

These results show that the vapour phase in equilibrium with liquid PF_3Cl_2 is principally monomeric, although it must be noted that the presence of a small degree of association or of dissociation might not be detectable by this experiment.

Considerable difficulty was encountered in obtaining reproducible results; in particular, a change in vapour pressure occurred slowly, which could not be explained in terms of reaction with any part of the apparatus or the admission of inadvertent traces of water. The lack of reproducibility may be connected with the ready formation of $[PCl_4^+][PF_6^-]$ (about which more will be said later); since it was observed that samples could not be evaporated without leaving a trace of a white solid residue, which appeared by the circumstances of its formation and its volatility to be $[PCl_4^+][PF_6^-]$. Satisfactory results for the vapour pressure were eventually obtained by limiting the time taken for equilibrium to be established before a pressure measurement was made to about 30 mins. and by employing three highly purified specimens in the course of the complete series of observations.

An examination of the melting point of solid PF_3Cl_2 showed that it lies in the range -125° to -130°

THE ELECTROLYTIC CONDUCTANCE OF PF_3Cl_2.

Reference has already been made to the existence of a compound of identical composition to PF_3Cl_2, namely solid ionic $[PCl_4^+][PF_6^-]$. This compound was shown by Kolditz to have a molar conductance of 90·9 ohm.$^{-1}$cm.^{2} mole.$^{-1}$ in acetonitrile solution at a concentration of 0·0420M.

It was of interest to study PF_3Cl_2 under similar conditions in order to investigate the possibility of a rearrangement of the molecular form to the ionic form occurring.

Acetonitrile is the most common solvent used in the study of electrolytic conductance of non-aqueous solutions of phosphorus pentahalides. The principle reason for employing acetonitrile is its very good solvent properties for this particular class of compound.

The conductance of PF_3Cl_2 in acetonitrile was examined in a specially designed pipette cell by means of which solutions could be manipulated without

Table 2. Variation of conductance with time.

Time (mins.)	κ x 10^4
0	1·04
5	2·26
15	2·43
25	3·73
55	4·21
70	4·37
85	4·37
0	5·18
10	5·35
20	5·51
50	7·12
90	7·94
100	8·42
130	8·42

coming into contact with a moist atmosphere. Two different solution concentrations were studied at 20° and the results are as follows:

C_m. (mole.litre^{-1})	0·0454	0·0905
$\kappa \times 10^4$	4·37	8·42
Λ_m(ohm.$^{-1}$cm.^{2} mole.$^{-1}$)	4·63	9·31

In each case the specific conductance of the solution was found to increase slightly with time, becoming constant some two hours after the solution was prepared; the value of the specific conductance at this constant value has been taken as the actual conductance value. The extent of the conductance drift with time is indicated in table 2.

The "conductance drift effect" in acetonitrile solutions has been noted by several workers: Harris & Payne (22) have reported the slight increase of the specific conductance of solutions of phosphorus pentabromide, and Popov and Skelly (23) observed the same effect occurring in a study of inter-halogen compounds. In the latter work, this effect was attributed to a slow ionisation of the type:

$$2ICl \rightleftharpoons I^+ + ICl_2^-.$$

The "conductance drift effect" found with acetonitrile solutions of PF_3Cl_2 may have a similar explanation.

In acetonitrile solution, PF_3Cl_2 may undergo a molecular dissociation process, which could yield phosphorus trifluoride and chlorine. However, investigation of the molar conductance of a pure sample of phosphorus trifluoride in acetonitrile gave a value of 0·26 $ohm.^{-1}$ $mole.^{-1}cm.^{2}$ at a molar concentration of 0·32 whilst solutions of halogens in acetonitrile are known to have very low conductance values. Thus, a molecular dissociation process can be eliminated as an explanation of the conductance values obtained.

In acetonitrile solution, the rearrangement of PF_3Cl_2 to $[PCl_4^+][PF_6^-]$ may occur, but the magnitude of the molar conductances (values should be doubled to compare with $[PCl_4^+][PF_6^-]$) shows that this has not occurred to completion if at all. The ions responsible for the conductance have not been identified but a simple ionisation process such as:

$$2PX_5 \rightleftharpoons [PX_4^+] + [PX_6^-]$$

where X represents either chlorine or fluorine, following the scheme observed with the simple phosphorus halides in this solvent (24)(22) would seem to be more favoured than the rearrangement.

The conductance of liquid PF_3Cl_2 was measured in an all-glass cell with small platinum electrodes, the cell being specially constructed to deal with small quantities of volatile material. The specific conductance was found to be less than 10^{-7} $ohm.^{-1}cm.^{-1}$ This clearly shows the molecular nature of the liquid form of PF_3Cl_2.

THE REACTION OF PF_3Cl_2 WITH WATER VAPOUR.

In this experiment, verification was sought for the reaction:

$$PF_3Cl_{2(g)} \quad + \quad H_2O_{(g)} \longrightarrow POF_{3(g)} \quad + \quad 2HCl_{(g)}$$

which is reported in the literature (13).

Since, in the reaction as quoted, there should be an increase in volume of 50%, a measurement of the pressure variation would provide direct confirmation.

The experiment was carried out in a bulb of approximate 300 ml. capacity at room temperature (19·2°). The bulb was filled with water vapour to a pressure corresponding to its vapour pressure at the temperature of the experiment, and an equal pressure of PF_3Cl_2. The vapour phases were allowed to react, the pressure of the system being observed by the spiral-gauge system, used in the vapour pressure determination. The pressure variation is recorded in table 3.

Vapour pressure of water at 19·2 = 16·69 mm.

=Vapour pressure of PF_3Cl_2 at -69·7°

(from V.P. equation)

Table 3. The Reaction Between PF_3Cl_2 and Water Vapour.

Time mins.	Pressure mm.
0	28·10
5	29·50
20	30·53
140	31·93
165	32·36
190	33·30

No effective change in pressure after 190 minutes.

Total theor. pressure on mixing, for no reaction
= 33·38 mm.

Increase in pressure of 50% requires p = 50·07 mm.

Thus after an initial pressure variation, the final pressure of the system corresponded to no net change in the volume of vapour present. The products of the reaction, present in part as droplets of liquid, were divided into a volatile and a non-volatile fraction; the former contained as shown by examination of the hydrolysed material, only chlorine, the latter only phosphorus and fluorine. This evidence supports the formation of a high-boiling oxyfluoride together with hydrogen chloride thus:

$$PF_3Cl_{2(g)} + H_2O_{(g)} \longrightarrow (POF_3)_{x(l)} + 2HCl_{(g)}$$

THE MASS SPECTRUM OF PF_3Cl_2.

In connection with the later studies on the thermal stability of PF_3Cl_2, a pure sample of PF_3Cl_2 was examined mass spectroscopically at an ionisation energy of 15 e.v. ; the mass peaks obtained are shown in table 4.

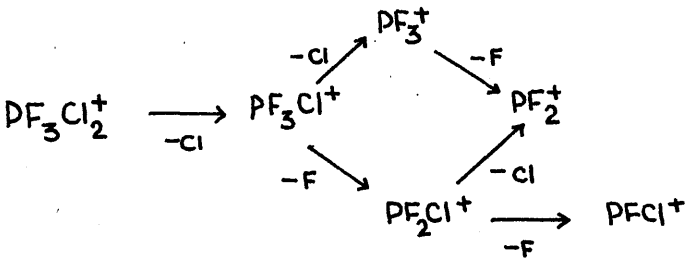
Table 4. Mass Spectrum of PF_3Cl_2 at 15 e.v.

Mass Peak	Assignment	Strength	Rqud. Mass.
35	Cl^+	s	35
37	Cl^+	s	37
69	PF_2^+	vw	69
85	$PClF^+$	w	85
87	$PClF^+$	w	87
88	PF_3^+	s	88
103	PF_2Cl^+	m	104
106	PF_2Cl^+	vs	106
123	PF_3Cl^+	vs	124
125	PF_3Cl^+	s	126
158	$PF_3Cl_2^+$	vw	158,(160,162)

The values taken for mass numbers of phosphorus oxygen, fluorine and chlorine were 31,16,19, and 35(75%) and 37(25%).

The species of mass 106 cannot exclusively be PF_2Cl^+ because of the lower relative peak height of mass 103, which is the adjacent peak corresponding, within the limits of experimental error, to the other chlorine isotope (^{35}Cl). It would be convenient to relate the peak at 106 in part to pyrolysis products such as phosphorus oxyfluoride or silicon tetrafluoride both of mass 104, but the difference in mass number is outside the error of the experiment and there is no evidence of hydrogen chloride or of other related fragments being present.

The mass peaks obtained can be interpreted according to the scheme:



The ionisation process leads largely to loss of chlorine; loss of fluorine appears only to occur from a mono chloro fragment, there being no evidence for $PF_2Cl_2^+$, or later fragments in the spectra.

THE REACTION BETWEEN PF_3Cl_2 AND AMMONIA.

Moissan (13) reported the reaction between PF_3Cl_2 and ammonia in the vapour phase as leading to the formation of phosphorus trifluorodiamide, $PF_3(NH_2)_2$. It was with a view to substantiating this report that a preliminary study of this reaction was carried out.

From a consideration of bond energy and steric effects, it seems reasonable to expect that in the PF_3Cl_2 molecule, the reactive sights are the two apical chlorine-phosphorus bonds. Consequently four volumes of ammonia were added for every volume of PF_3Cl_2 used.

The reactants were first condensed under liquid oxygen and then allowed to warm up slowly until reaction was complete. Examination of the volatile phase which results showed that the I.R. spectrum indicated that ammonia only was present; subsequent experiments invariably gave a residual pressure of ca. 10% of the original volume of ammonia added. The main bulk of the reaction product was present as a white solid material. The X-ray powder diagram of this solid material gave results which are set out in table 5; the

Table 5. The X-Ray Powder Data for the Product of Reaction Between PF_3Cl_2 and Ammonia.

$d_{\text{Å}}$	d_{NH_4Cl}	d_{NH_4F}
5·47		
5·31		
4·92		
3·81	3·85	3·85
		3·59
		3·39
3·16		
3·02		
2·70	2·73	
		2·62
2·22	2·23	2·22
2·10		
2·02		2·00
1·72	1·72	
1·57	1·58	
		1·49
		1·45
		1·42

Table 5. (Contd)

$d_{Å}$	d_{NH_4Cl}	d_{NH_4F}
1·35	1·35	1·34
1·26	1·29	1·27
		1·24
1·21	1·22	
1·16	1·16	
1·11	1·11	

d-spacings of ammonium chloride and ammonium fluoride are given for reference (25)(26). From the table it is clear that ammonium chloride but not ammonium fluoride is present as a product of reaction. The powder pattern of $[NH_4^+][PF_6^-]$ was obtained and is included in the Appendix; reference to this pattern and to the patterns of the solids $[PCl_4^+][PF_6^-]$ and $[PCl_4^+]F^-$ showed that these substances did not exist as products of reaction. A sample of the solid reaction product was hydrolysed by dilute acid and the hydrolysate tested for the presence of $[PF_6^-]$ ion by addition of Nitron reagent. A fawn-coloured solid was obtained with a melting point of 228° (Kolditz: Nitron-$[PF_6^-]$ compound M.P. 229°); the I.R. spectrum and X-ray powder diagram showed it to be identical with the Nitron-$[PF_6^-]$ complex.

A partial separation of the solid reaction products was attempted by sublimation at 80-90° and 10^{-2}mm. pressure. Sublimation was accompanied by the evolution of ammonia, which was identified by its I.R. spectrum. The I.R. spectrum of both the residue and the sublimate showed them to contain ammonium chloride and compound(s) containing P-F bonds. The spectrum of the residue also indicated the appearance of a hitherto absent frequency at $3320cm.^{-1}$ This frequency may be due to a $P-NH_2$ or $P=NH$ group. The formation of an imine group could be linked with the evolution of ammonia found on sublimation; elimination of ammonia intramolecularly would produce imine type bonds whilst intermolecular elimination could lead to formation of polymeric material. The observation that the theoretical quantity of ammonia does not react initially would seem to suggest a similar type of imine or chain formation as that discussed when sublimation is attempted.

No further work was carried out on this reaction and no conclusions can be drawn as to the products of reaction without further investigation.

THE PYROLYSIS OF PF_3Cl_2.

DISCUSSION OF THE EXPERIMENTAL RESULTS.

Breakdown of the molecule PF_3Cl_2 by pyrolysis might proceed by at least two types of reaction: disproportionation might occur giving rise to phosphorus V compounds of greater stability or simple dissociation yielding phosphorus trihalide and halogen may take place.

Moissan studied the action of heat on PF_3Cl_2 and reported that the system underwent disproportionation at 200-250° giving gaseous phosphorus pentafluoride and solid phosphorus pentachloride:

$$5PF_3Cl_2 \longrightarrow 2PCl_5 + 3PF_5$$

It was decided to re-investigate the pyrolysis in order to examine the temperature stability of PF_3Cl_2 and the nature of any reaction which occurs.

In general, heating a gaseous sample of PF_3Cl_2, up to a temperature of ca.200° followed by slow cooling to 20°, resulted in an overall pressure reduction of 45-50%; also a white solid was invariably deposited on the walls of the apparatus.

The investigation of the pyrolysis was begun by making a study of the pressure-temperature variation of a sample heated slowly to 207° in rigorously dried apparatus and cooled slowly to 20°. It was found that the system obeyed Charles' Law in the temperature range 20-150°. Above 150°, the slope of the pressure-temperature curve was found to deviate from the theoretical line. Assuming complete conversion above 150° to the products suggested by Moissan, and comparing the observed pressure with that calculated for a mixture of phosphorus pentafluoride and phosphorus pentachloride present in the required ratio, it was found that the calculated value exceeded the observed value by a large amount. Thus Moissan's interpretation cannot be accepted as being correct.

Studies of the mass spectra of phosphorus pentachloride and of a new compound P_2Cl_9F have shown the presence of dimeric units in the vapour phase. In this light, it is perhaps reasonable to postulate that some degree of association occurs with PF_3Cl_2 also. However, in the course of the vapour pressure study of PF_3Cl_2 molecular weight determination gave the result 159 ± 1, expected of a monomeric unit. Consequently, although the possibility of association must be admitted, the extent to which it can occur must be very small. It follows that the contribution which such a process would make to the pressure variation must also be of very little consequence.

The fact that PF_3Cl_2 obeys Charles' Law up to a temperature of 150° eliminates the possibility of dissociation such as:

$$PF_3Cl_2 \rightleftharpoons PF_3 + Cl_2.$$

occurring to any appreciable degree. This conclusion is in marked contrast to the behaviour of phosphorus pentachloride which is dissociated to an extent of 10-15% at 150°. Above this temperature, however, it is much more difficult to draw any conclusions concerning the existence of dissociation of the PF_3Cl_2 molecule.

The kinetic studies of Wilson have shown that the rate of reaction of phosphorus trifluoride with chlorine is very small and decreases markedly with temperature, at least over the low temperature ranges. Furthermore, in the present work, the existence of phosphorus trifluoride vapour could have been unambiguously detected by examination of the I.R. spectrum. The "quenched" pyrolysis experiment described below in greater detail, would be most likely to contain phosphorus trifluoride and chlorine from the dissociation of PF_3Cl_2 if it occurred to an appreciable extent. However the I.R. spectrum, showed that phosphorus trifluoride was, in fact, absent.

It would seem then from these observations that the dissociation process $PF_3Cl_2 \rightleftharpoons PF_3 + Cl_2$ does not play a significant part in the pressure temperature variation which occurs during pyrolysis, although it will require further study in order to establish, unambiguously, the complete absence of this dissociation

There is a possibility, however, that an alternative disproportionation reaction could occur, yielding products different from those suggested by Moissan. Consequently, after separation of the solid and the volatile reaction products by pumping off the latter at room temperature, a more detailed study of both vapour and solid phases was undertaken.

By reference to published patterns, the solid phase was shown by X-ray powder photography to be a mixture of the solids, $[PCl_4^+][PF_6^-]$ and $[PCl_4^+]F^-$ (15)(16). After alkaline hydrolysis of the mixed solid, the presence of the $[PF_6^-]$ ion was confirmed by complex formation with Nitron. Analysis of the solid compound coupled with the foregoing observations indicated that the solid had the composition 45%$[PCl_4^+]F^-$; 55%$[PCl_4^+][PF_6^-]$. The results of pH titration of the solution produced by acid hydrolysis of the solid could be interpreted in terms of the presence of hydrofluoric acid, hydrochloric acid, phosphoric acid and hexafluophosphoric acid, in the relative amounts required for the composition cited above. Moreover, the apparent molecular weight calculated from this titration was of the correct magnitude. The existence of the $[PF_6^-]$ ion in the solution after titration was again confirmed by complex formation with Nitron.

Thus, at this stage, it can be concluded that

PF_3Cl_2 is neither dissociated or associated to any appreciable extent, below a temperature of 150°. Above this temperature, decomposition occurs which may lead either to the formation of PCl_4F and phosphorus pentafluoride or alternatively to the formation of $[PCl_4^+][PF_6^-]$ which would then undergo dissociation to PCl_4F and phosphorus pentafluoride (16). Consideration of this possible reaction required a more detailed study of the products of pyrolysis.

Examination of the volatile products of pyrolysis was begun by an attempt to resolve the components by fractional distillation in vacuo; two fractions were obtained. From its I.R. spectrum, the lower boiling fraction was found to contain silicon tetrafluoride, phosphorus oxyfluoride and some phosphorus pentafluoride while the higher boiling fraction contained PF_3Cl_2 and some unidentified material. I.R. examination of the vapour phase in equilibrium with the solid product of hydrolysis held at 40° (i.e. at a temperature at which disproportionation does not occur) showed the presence of PF_3Cl_2 but in addition bands were found at the same frequencies as those unaccounted for in the examination of the volatile phase, mentioned above. The vapour which is in equilibrium with the solid $[PCl_4^+][PF_6^-]$ in the temperature range 0°-40° is PF_3Cl_2 and it is thus likely that the unallocated frequencies are due to vapour molecules in equilibrium with the other solid produced $[PCl_4^+]F^-$; that is, possibly PCl_4F.

This observation together with the conclusions reached from a study of the I.R. spectrum of the volatile phase of the pyrolysis products showed that after cooling to room temperature, phosphorus oxyfluoride, phosphorus pentafluoride, silicon tetrafluoride, PF_3Cl_2 and PCl_4F exist in the gaseous mixture. Molecular weight measurements coupled with phosphorus and chlorine analysis gave the composition of this volatile phase as phosphorus pentafluoride 9·1%; silicon tetrafluoride 22·8%; phosphorus oxyfluoride 45·6% and PCl_4F 22·8%. These results, in combination with the reduction in pressure of 45% found in this experiment, make it possible to confirm the composition of the solid phase found by analysis. In fact, there was very good agreement between the composition calculated on this basis and the direct analytical results. Although PF_3Cl_2 was a component of the volatile phase, it was only present in a very small amount corresponding to the vapour pressure of $[PCl_4^+][PF_6^-]$ at room temperature.

The mass spectrum of the volatile products yielded fragmentation patterns which gave further evidence for the existence of phosphorus pentafluoride, phosphorus oxyfluoride, silicon tetrafluoride, PF_3Cl_2 and PCl_4F in the volatile products. Also, it appears that when PF_3Cl_2 is heated, it remains unchanged, obeying Charles' Law to a temperature of ca.150°. Thereupon, a disproportionation process occurs by which phosphorus pentafluoride and PCl_4F are formed according to the equation

$$2PF_3Cl_2 \longrightarrow PCl_4F + PF_5.$$

As the temperature is raised further there is attack by the phosphoruspentafluoride on the glass apparatus yielding phosphorus oxyfluoride and silicon tetrafluoride thus:

$$2PF_5 \xrightarrow{SiO_2} POF_3 + 0{\cdot}5SiF_4$$

The extent of this reaction, furthermore, is found to be a function of temperature rather than of time.

Cooling the system to 20°, results in the formation of $[PCl_4^+]F^-$ and $[PCl_4^+][PF_6^-]$. However, no conclusion can be arrived at concerning the method of formation of the $[PCl_4^+][PF_6^-]$. Clearly it could result either from a combination of molecular PCl_4F or of ionic $[PCl_4^+]F^-$ with phosphorus pentafluoride. The latter reaction has been reported by Kolditz to occur at 135° (16).

Now if the system above 150° involves phosphorus pentafluoride and PCl_4F, it is reasonable to suggest that the recombination reaction which takes place on slow cooling to 20° might be largely prevented by rapid cooling. Furthermore, if PF_3Cl_2 is present above 150°, this might also be detected by "quenching" the system and might thus differentiate it from PF_3Cl_2 formed from $[PCl_4^+][PF_6^-]$. Accordingly a quenching experiment was carried out by rapidly cooling a sample from 210° to -80° resulting in the formation of noticeable less of the solid phase.

Further, the pressure decrease in this experiment was only 15%. Immediate measurement of the I.R. spectrum showed it to be similar to that of the volatile phase in the slow cooling experiment with one important exception: no frequencies corresponding to PF_3Cl_2 were found. However, after allowing the system to stand for some thirty minutes and then re-examining the I.R. spectrum, it showed the presence of PF_3Cl_2. It was concluded from this latter observation that the quenching experiment was effective in preventing recombination of PCl_4F and phosphorus pentafluoride but that this process did take place when the system was allowed to stand. This experiment provides conclusive proof that the disproportionation reaction which occurs above 150° leads to the formation of PCl_4F and phosphorus pentafluoride. Kolditz (16) has made reference to the formation of $[PCl_4^+][PF_6^-]$ by combination of $[PCl_4^+]F^-$ with phosphorus pentafluoride. It is claimed that combination, accompanied by the formation of PF_3Cl_2, occurs rapidly at 135° under pressure, whilst at 50° the reaction is complete in 5-10 minutes. No mention is made of a reaction occurring between molecular PCl_4F and phosphorus pentafluoride. Four discrete forms in which PCl_4F can occur have been recognized viz: as an ionic solid, $[PCl_4^+]F^-$, as a covalent liquid, PCl_4F, as molecular PCl_4F in the vapour phase, and as solidified PCl_4F at -67°. Disproportionation of $[PCl_4^+]F^-$ is said to yield, after melting and cooling, $[PCl_4^+][PF_6^-]$ and phosphorus pentachloride. Measurement of the vapour density of $[PCl_4^+]F^-$ at 190° using the Victor Meyer method, is reported to show that the vapour is completely dissociated; two dissociation processes are discussed:

$$[PCl_4^+]F^- \longrightarrow PCl_4F \rightleftharpoons PCl_3 + ClF$$

$$[PCl_4^+]F^- \longrightarrow PCl_4F \rightleftharpoons PCl_2F + Cl_2$$

the second scheme is favoured by Kolditz as the first involves formation of a Cl-F bond.

These observations are rather difficult to reconcile in the light of the results emerging from the present studies.

Firstly, with regard to the formation of $[PCl_4^+][PF_6^-]$ it seems reasonable to suggest that phosphorus pentafluoride could react more readily with PCl_4F than with $[PCl_4^+]F^-$ since in the latter case additional energy would be required to offset the lattice energy of the solid. Thus the reaction might take the form

$$PF_{5(g)} \quad + \quad PCl_4F_{(g)} \quad \longrightarrow \quad [PCl_4^+][PF_6^-]_{(s)}.$$

This would be accompanied by formation of solid $[PCl_4^+]F^-$ thus:

$$PCl_4F_{(g)} \quad \longrightarrow \quad [PCl_4^+]F^-_{(s)}.$$

No indication of the presence of a liquid form of PCl_4F was found in the pyrolysis studies, the analytical results being compatible with the presence only of solid and gaseous forms. This observation, however, might be expected since the reported boiling point of liquid PCl_4F is 67° and it would thus have a high vapour pressure at room temperature. Consequently any liquid PCl_4F which initially formed would almost certainly vapourize unless the volume of the vessel was small.

With reference to the reported disproportionation of $[PCl_4^+]F^-$ at 161° yielding $[PCl_4^+][PF_6^-]$ and phosphorus pentachloride the following comment can be made. It was observed in the pyrolysis study that when deviation from Charles' Law occurred above 150°, the pressure-temperature relationship could be described by a straight line. Furthermore on lowering the temperature to 20° and then raising it again to ca.170°, this line was found to be completely reproducible. This would not be expected if disproportionation of the $[PCl_4^+]F^-$ initially formed, yielded $[PCl_4^+][PF_6^-]$ and phosphorus pentachloride. In addition, no evidence of phosphorus pentachloride was found in the X-ray powder diagram of the solid products from pyrolysis.

The extent of the pressure increase on pyrolysis above 150° is particularly significant when the determination of the vapour density is considered. This pressure increase would be built up with the formation of phosphorus oxyfluoride and silicon tetrafluoride along with PCl_4F and its dissociation products; it is improbable that dissociation of phosphorus pentafluoride would occur. However, the magnitude of this pressure increase at 190° is considerably smaller than that required for total dissociation of PCl_4F, as observed by Kolditz, and can be taken as direct evidence to the contrary. It should be pointed out that the dissociation of PCl_4F would be affected by the presence of phosphorus oxyfluoride and silicon tetrafluoride, which would act as diluent gases. It is unlikely, however, that this effect would be sufficient to explain the difference between the small degree of dissociation found at 190° and the complete dissociation reported by Kolditz.

The pyrolysis system involves several reactions which are occurring at the same time and under such conditions the isolated equilibria, which Kolditz has observed, may not be applicable.

THE STABILITY OF PF_3Cl_2 AT ROOM TEMPERATURE.

As a corollary to the studies of PF_3Cl_2 vapour at elevated temperatures, the stability of the gas at room temperature was investigated. Pure samples of PF_3Cl_2 were sealed up in suitable glass bulbs and stored at room temperature. After several days, the bulbs were examined and found to contain varying amounts of a white solid material. The X-ray powder diagram of this white solid showed it to be a mixture of $[PCl_4^+][PF_6^-]$ and $[PCl_4^+]F^-$, as was also found in the pyrolysis studies. Analysis of the solid showed it to consist of 86% $[PCl_4^+][PF_6^-]$ and 14% $[PCl_4^+]F^-$; this is to be compared with 56% $[PCl_4^+][PF_6^-]$ and 44% $[PCl_4^+]F^-$ found in the pyrolysis studies. A significant observation was the fact that the speed with which solid formation took place was dependent on the extent to which the storage vessels were initially baked out; storage of PF_3Cl_2 in an undried vessel was very rapidly accompanied by formation of the solid. Even the most intensive drying of the apparatus, however, could not prevent solid being formed.

The rate at which the reaction took place at room temperature was next investigated by observing the variation with time of the pressure of the system, using an all-glass apparatus very similar to that used in the pyrolysis work. After recording pressure-time measurements over a period of thirty-five days, the experiment was terminated; the pressure of the system, at this stage, was found to be 52% of its initial value. A graphical interpretation of the results showed that the reaction which occurs could be adequately described by zero-order kinetics over the pressure range studied. The reaction which occurs may therefore be initiated on the glass surface of the apparatus. This result, together with the "baking-out effect" found suggests that the reaction which occurs on storing PF_3Cl_2 vapour at 20° is connected with traces of water absorbed on the glass surface of the apparatus. This might result in some hydrolysis of PF_3Cl_2, forming hydrogen halide which might catalyse further reaction. It is possible that this explanation could be extended to explain, in part, the reaction which occurs on pyrolysis, since both pyrolysis and storage experiments yield very similar reaction products. That the pyrolysis reaction takes place very much more rapidly may be due to additional water molecules being made available, by the elevated temperatures, to take part in the reaction.

Investigation of the vapour phase which is formed on storing PF_3Cl_2 at 20°, was confined to a study of I.R. spectra. The spectra were found to be very similar to that of the vapour phase resulting from pyrolysis; frequencies ascribed to phosphorus oxyfluoride, phosphorus pentafluoride, PF_3Cl_2, silicon tetrafluoride and probably PCl_4F were found. Thus, the reaction occuring at 20° involves the disproportionation of PF_3Cl_2 according to the scheme:

$$2PF_3Cl_2 \longrightarrow PF_5 + PCl_4F.$$

the reaction occuring slowly. Subsequent combination of PCl_4F with phosphorus pentafluoride yields $[PCl_4^+][PF_6^-]$, accompanied by the deposition of $[PCl_4^+]F^-$ viz:

$$PCl_4F + PF_5 \longrightarrow [PCl_4^+][PF_6^-]$$

$$PCl_4F \longrightarrow [PCl_4^+]F^-$$

The relatively larger amounts of $[PCl_4^+][PF_6^-]$ found in the storage studies may be explained in the following way: the extent to which phosphorus pentafluoride attacks the glass apparatus at 20° will be very much less than at the temperatures of pyrolysis, i.e. 150-220°. There will then be more phosphorus pentafluoride available to combine with PCl_4F, and thus formation of $[PCl_4^+][PF_6^-]$ will occur to a greater extent than in the pyrolysis reaction.

EXPERIMENTAL RESULTS.

THE EFFECT OF HEAT ON PF_3Cl_2.

The inquiry into the effect of heat on PF_3Cl_2 was opened by making a study of the pressure variation with temperature which occurred when a pure sample of PF_3Cl_2 was heated in an all-glass system.

Two experiments were carried out, the pressure-temperature variations being recorded in tables 6 and 7 and represented graphically in figures 3 and 4. Each experiment was conducted over a period of 9 to 10 days; each individual day is bounded by chain lines in the tables of results. In the second experiment, a detailed investigation of the behaviour of the system in the temperature range 20°-100° was carried out.

It was found that PF_3Cl_2 behaved as an ideal gas until a temperature of ca.150° was reached, obeying Charles' Law for ascending and descending temperatures. Between 150° and 170° the system deviated from the theoretical line, the pressures being higher than those expected. Further temperature increase gave pressure variations which could be represented by a linear relationship which was found to describe the system over the temperature range ca.70°-220° for both ascending and descending temperatures. In the second experiment, investigation was continued from 70° to 20° and then from 20° to 150°. The curves obtained in this region were found to exhibit a hysteresis effect; repeating the measurements over the range 20° to ca.120° did not give identical results, the second set of pressure measurements being higher. Raising the temperature above 120° gave pressure values which lay on the straight line which was first obtained after deviation from the Charles' Law line had occurred.

At temperatures below ca.70° a white solid material could be seen deposited on the walls of the apparatus.

In order to compare the results obtained from both experiments, each pressure value was converted to a ratio by dividing it by the initial pressure of the system at 200°. Each pressure ratio was then plotted against temperature; the results are recorded in tables 8 and 9 and shown graphically in figure 5. From the graph it is seen that there is good agreement between the two experiments.

PYROLYSIS EXPERIMENTS.

Table 6. The Pyrolysis of PF_3Cl_2. Experiment I.

Temp °C	Pressure mm.	Temp °C	Pressure mm.
-180°	0·0	104·7	157·52
18·0	121·35	107·0	158·00
39·0	129·92	112·5	160·30
49·2	135·06	116·5	161·55
68·9	140·93	116·5	163·00
79·7	147·16	121·5	164·56
85·5	152·50	127·1	167·01
72·7	144·44	134·1	170·45
66·5	142·00	141·0	173·32
55·5	138·07	150·9	177·44
43·2	132·34	121·6	165·26
76·0	145·54	100·9	155·73
81·0	147·43	74·6	145·05
85·1	148·96	156·5	181·60
89·2	151·16	160·2	184·03
94·0	153·08	167·5	188·46
98·6	153·73	160·4	186·45
63·5	140·17	147·2	179·22
22·0	122·86	133·0	172·87
102·0	156·17	120·0	166·30

Table 6.(contd.)

Temp °C	Pressure mm.	Temp °C	Pressure mm.
120·0	166·20	114·2	162·99
141·0	175·73	184·0	197·19
165·5	187·42	193·2	203·31
181·0	195·21	175·4	191·27
170·0	190·14	153·0	181·52
154·0	182·83	136·0	173·18
144·3	178·37	121·5	167·20
131·0	173·09	84·2	149·57
127·0	169·79	68·5	140·71
114·2	163·76	63·0	134·16
		49·0	127·70

Table 7. The Pyrolysis of PF_3Cl_2. Experiment II.

Temp °C	Pressure mm.	Temp °C	Pressure mm.
17·0	260·89	159·4	400·02
20·0	264·16	145·5	386·36
50·0	291·29	131·8	370·54
71·6	310·28	110·0	347·90
89·4	326·09	91·2	330·54
108·5	343·66	141·0	379·27
133·4	365·79	169·5	408·67
142·6	374·94	152·8	391·31
119·8	353·74	119·0	358·16
93·8	331·03	102·9	340·43
92·8	330·50	89·0	327·00
136·8	370·99	78·8	317·36
150·0	383·75	67·0	302·52
162·4	396·38	58·0	289·09
176·5	411·70	46·6	273·30
181·8	418·01	32·0	250·35
195·0	430·28	25·3	234·30
207·0	444·21	20·0	210·20
195·0	436·19	60·0	246·83
175·6	417·01	79·0	263·80

Table 7.(contd.)

Temp °C	Pressure mm.	Temp °C	Pressure mm.
98·3	295·59	43·7	274·73
111·5	350·51	37·5	264·88
123·0	360·30	20·2	221·50
145·6	384·40	52·2	247·58
166·5	405·14	74·7	272·76
149·8	387·50	95·5	301·07
130·0	370·15	95·5	304·27
140·1	342·08	95·5	305·78
78·8	314·74	103·8	333·08
61·5	295·28	125·5	366·48
51·5	283·51	29·2	243·28
		15·5	164·72

Fig.3. The Pyrolysis of PF_3Cl_2. Expt. I.

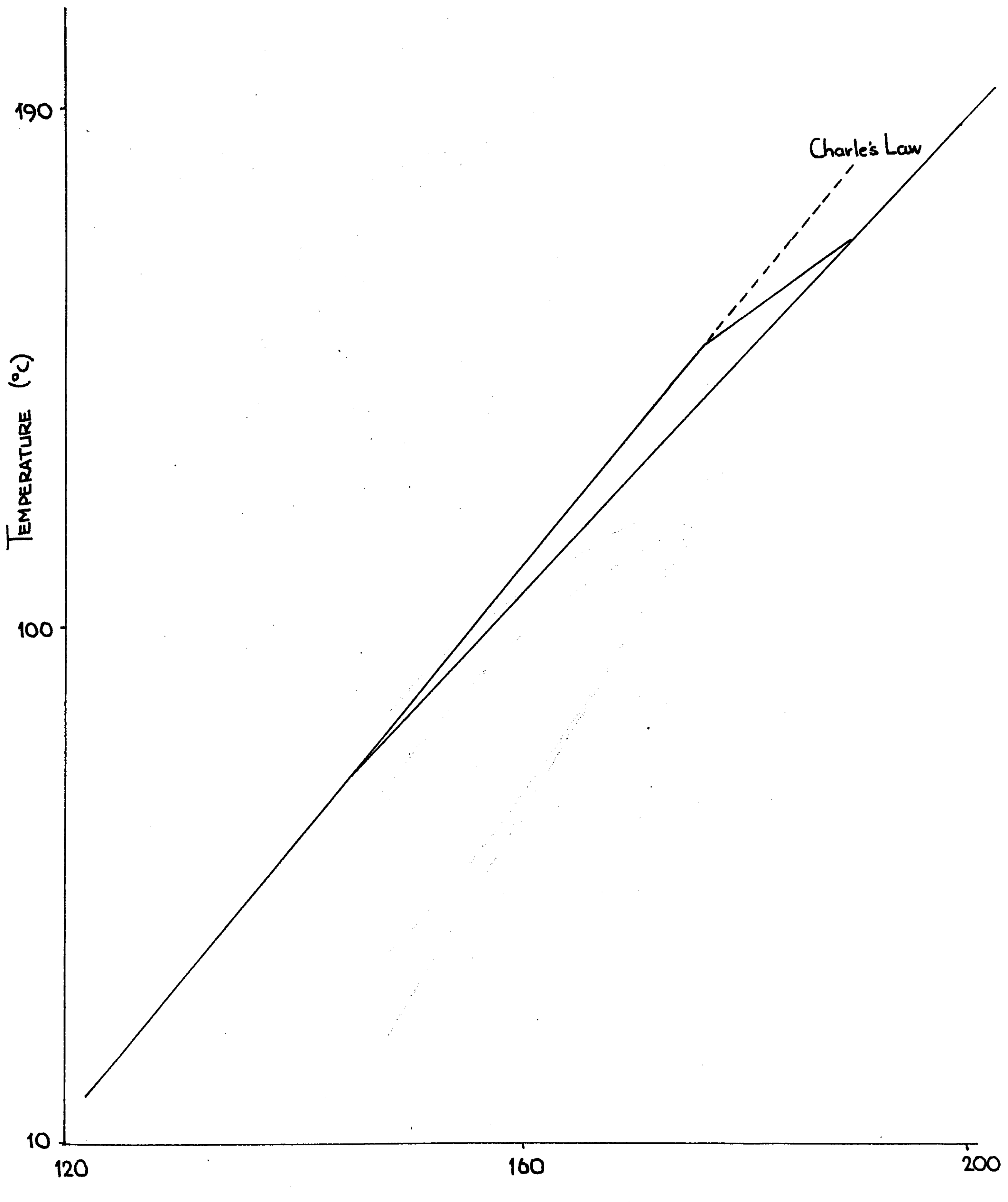


Fig. 4. The Pyrolysis of PF_3Cl_2. Expt. II.

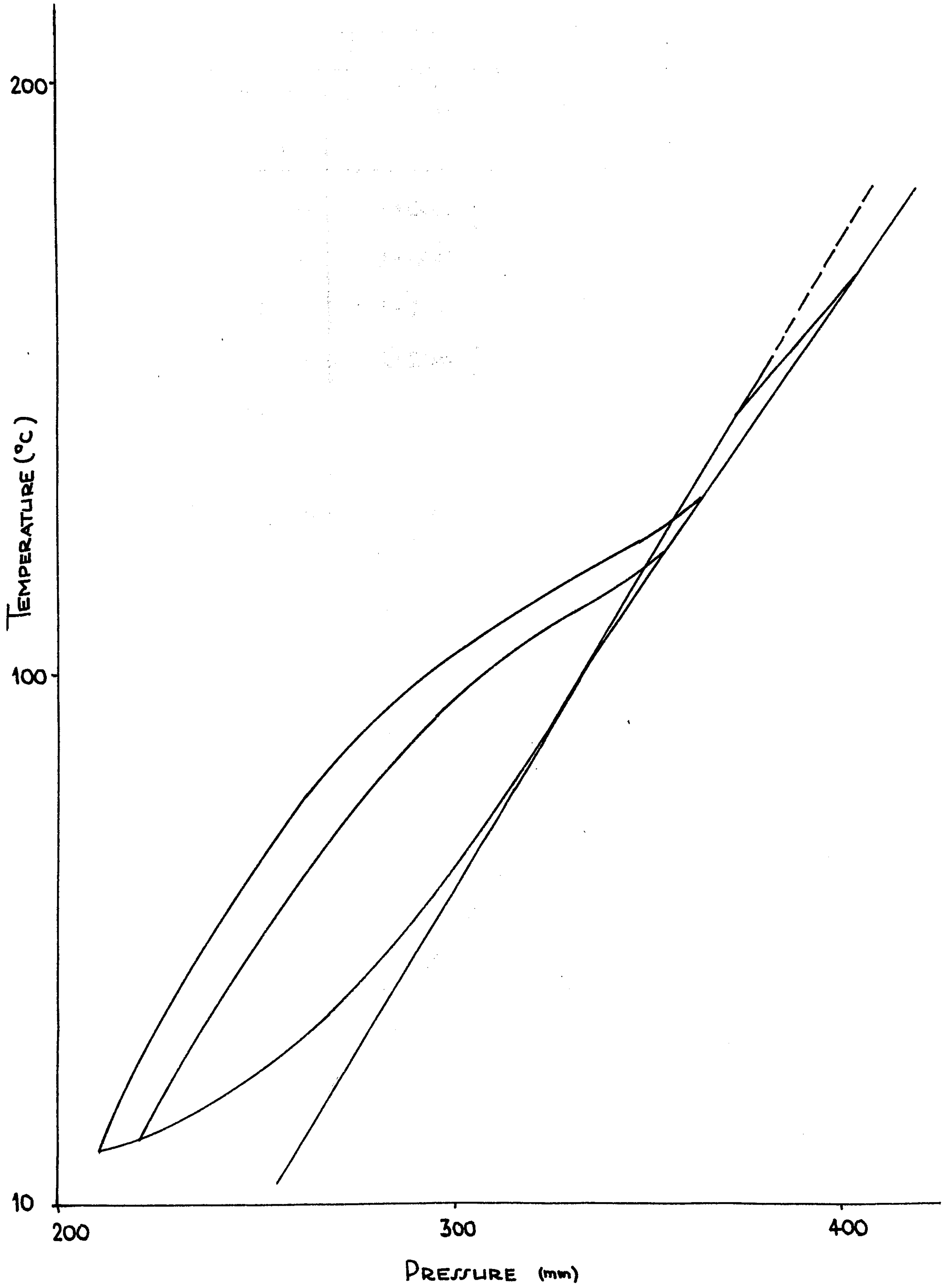


Table 8. Comparison Between Expts. I & 11 : Expt.I.

Pressure at 20°C = 121·86 mm = P_s.

Temp °C	Press mm.	P/P_s	Temp °C	Press mm.	P/P_s
39·0	129·92	1·066	112·5	160·30	1·315
49·2	135·06	1·108	116·5	161·55	1·326
68·9	140·93	1·156	121·5	164·56	1·350
79·7	147·16	1·208	127·1	167·01	1·370
85·5	152·50	1·251	134·1	170·45	1·399
72·7	144·44	1·185	141·0	173·32	1·422
66·5	142·00	1·165	150·9	177·44	1·456
55·5	138·07	1·133	121·6	165·26	1·356
43·2	132·34	1·086	100·9	155·73	1·278
76·0	145·54	1·194	74·6	145·05	1·190
81·0	147·43	1·209	156·5	181·60	1·490
85·1	148·96	1·222	160·2	184·03	1·510
89·2	151·16	1·240	167·5	188·46	1·547
94·0	153·08	1·256	160·4	186·45	1·530
98·6	153·73	1·262	147·2	179·22	1·471
63·5	140·17	1·150	133·0	172·87	1·419
22·0	122·86	1·008	120·0	166·30	1·365
102·0	156·17	1·282	141·0	175·73	1·442
104·7	157·52	1·293	165·5	187·42	1·538
107·0	158·00	1·296	181·0	195·21	1·602

Table 8. (contd.)

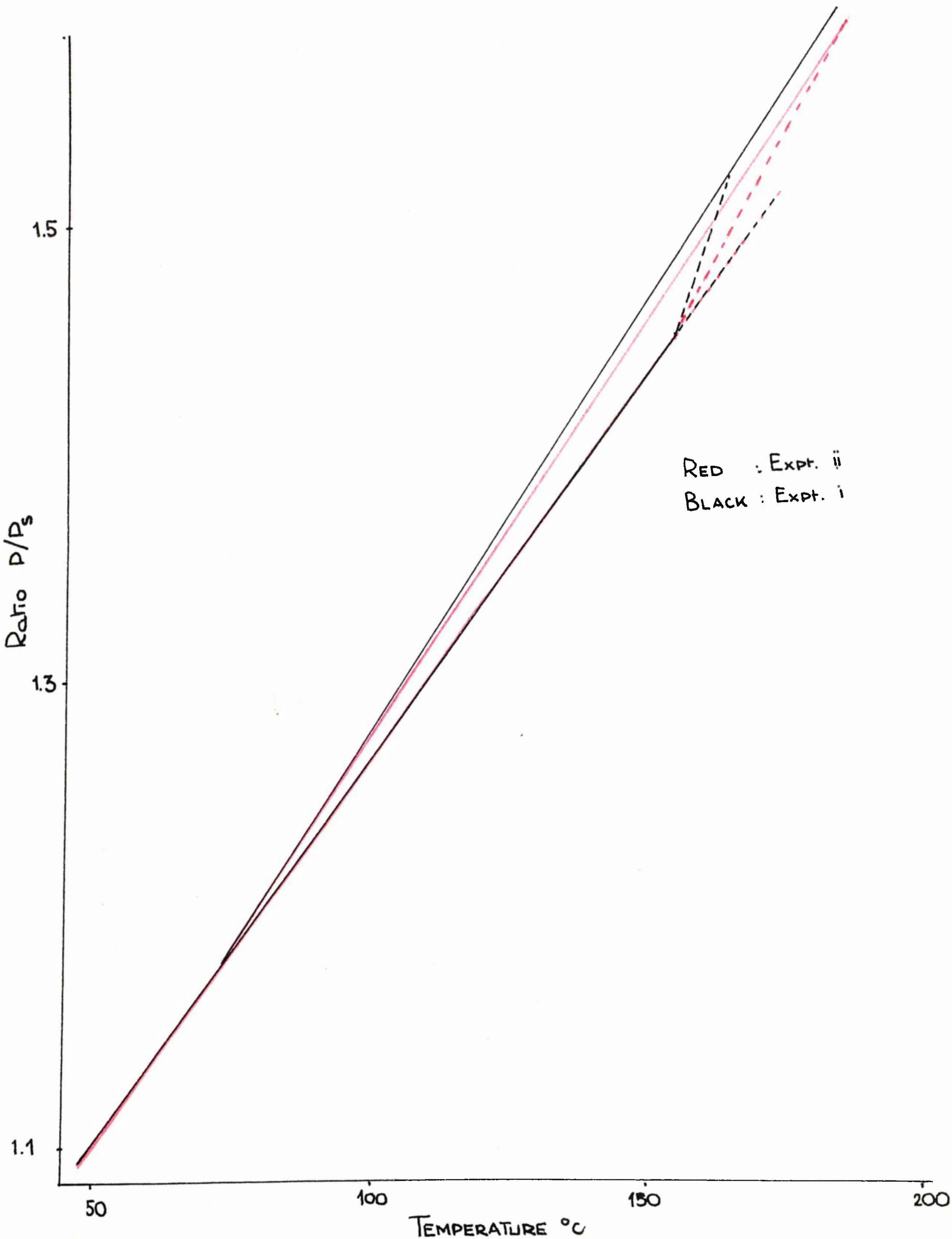
Temp °C	Press mm.	P/P_s	Temp °C	Press mm.	P/P_s
170·0	190·14	1·560	153·0	181·52	1·490
154·0	182·83	1·500	136·0	163·18	1·341
144·3	178·37	1·464	121·5	167·20	1·372
131·0	173·09	1·420	84·2	149·57	1·227
127·0	169·79	1·393	68·5	140·71	1·155
114·2	163·76	1·344	63·0	134·16	1·101
175·5	141·27	1·569	49·0	127·70	1·048

Table 9. Comparison Between Expt. I and II : Expt. II.

Pressure at 20°C = 264·16mm = P_s.

Temp °C	Press mm.	P/P_s	Temp °C	Press mm.	P/P_s.
20·0	264·16	1·000	145·5	386·36	1·463
50·0	291·29	1·103	131·8	370·54	1·403
71·6	310·28	1·175	110·0	347·90	1·317
89·4	326·09	1·234	91·2	330·54	1·251
108·5	343·66	1·301	141·0	379·27	1·436
133·4	365·79	1·385	169·5	408·67	1·547
142·6	374·94	1·420	152·8	391·30	1·481
119·8	353·74	1·340	119·0	358·16	1·356
93·8	331·03	1·253	102·9	340·43	1·289
92·8	330·50	1·251	111·5	350·50	1·327
136·8	370·99	1·404	123·0	360·50	1·364
150·0	383·75	1·453	145·0	384·40	1·455
162·4	396·38	1·500	166·5	405·14	1·534
176·5	411·70	1·559	149·8	387·50	1·467
181·8	418·01	1·582	130·0	370·15	1·401
175·6	417·01	1·579	104·1	342·08	1·300
159·4	400·02	1·514	78·8	314·74	1·192

Fig. 5. Comparison between Expts. I and II.



DISCUSSION OF THE EXPERIMENTAL RESULTS.

If deviation from Charles' Law was the result of a disproportionation reaction:

$$5PF_3Cl_2 \longrightarrow 2PCl_5 + 3PF_5$$

- the magnitude of the pressure increase to be expected can be calculated by making use of published data (27) on the vapour phase dissociation of phosphorus pentachloride, which is described by the following equation:

$$\log_{10}K_p = \frac{20,000T^{-1}}{4\cdot57} + 1\cdot75\log_{10}T + 6\cdot66$$

Values of $\log_{10}K_p$ were calculated for a suitable temperature range and are set out in table 10.

At temperatures ca.150°, the total pressure of the system can be expressed thus: -

$$P_T = P_{PCl_5} + P_{PCl_3} + P_{Cl_2} + P_{PF_5}$$

and $P_{PF_5} = 0\cdot6P_{PF_3Cl_2}$.

$P_{PF_3Cl_2}$ is the pressure which the system would have if no disproportionation had taken place. The total pressure was calculated in this way and compared with the observed pressure. These results are set out in table 11 and

Fig 6. Interpretation of the Pyrolysis Reaction as

$5PF_3Cl_2 \longrightarrow 2PCl_5 + 3PF_5$.

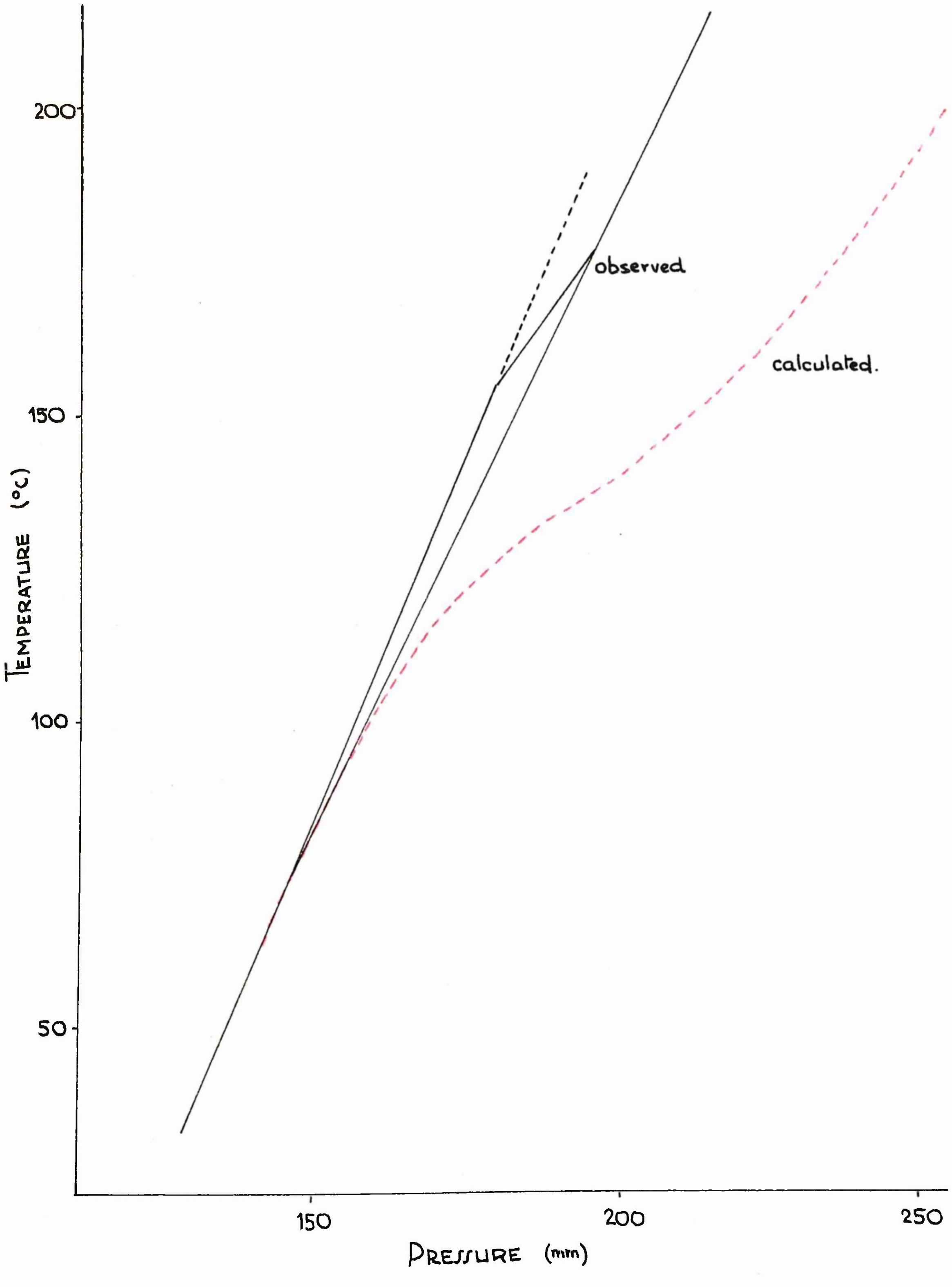


Table 10. Equilibrium constant for the dissociation:

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$.

Temp °C	$Log_{10}K_p$.
25	-3·697
50	-2·498
75	-1·470
100	-0·573
125	0·212
150	0·910
175	1·532
200	2·089

Table 11. Calculation of the Total Pressurefor the Reaction

$5PF_3Cl_2 \longrightarrow 3PF_5 + 2PCl_5 \rightleftharpoons 2PCl_3 + 2Cl_2$.

T°C	$P_{PF_3Cl_2}$	P_{PCl_5}	P_{Cl_2, PCl_3}	P_{PF_5}	P_{total}	$P_{obsvd.}$
25	124·0	49·21	0·59	74·40	124·2	124·3
50	134·7	53·88	0·82	80·82	135·5	135·0
75	144·9	56·57	2·77	86·94	146·3	146·1
100	155·8	58·40	7·84	93·48	159·6	157·1
125	166·1	56·82	19·24	99·66	176·7	168·8
150	176·5	34·60	72·0	105·90	212·5	180·6
175	187·7	29·78	91·78	112·62	233·8	192·5
200	197·9	24·31	110·70	118·74	252·8	204·2

figure 6. It is quite clear from these results that the pyrolysis of PF_3Cl_2 cannot be explained in terms of Moissan's disproportionation scheme. It is possible to formulate a number of disproportionation reactions which do not involve phosphorus pentachloride. These can be set out in the following forms:

$$(1) \quad 2PF_3Cl_2 \longrightarrow PCl_4F + PF_5$$

$$(2) \quad 3PF_3Cl_2 \longrightarrow 2PCl_3F_2 + PF_5$$

$$(3) \quad 2PF_3Cl_2 \longrightarrow PCl_3F_2 + PF_4Cl$$

$$(4) \quad 5PF_3Cl_2 \longrightarrow 3PClF_4 + PCl_4F + PCl_3F_2.$$

It is shown (see later) that a product of the pyrolysis reaction is phosphorus pentafluoride and thus reactions (3) and (4) can be eliminated. From a consideration of the results of the analysis of the products of the pyrolysis reaction, it is very likely that reaction (1) is the one which takes place.

No details are available regarding the vapour phase dissociation of PCl_4F. If the disproportionation scheme (1) is adopted, however, values of the equilibrium constants for the dissociation of PCl_4F in the vapour phase can be determined. The dissociation of a PCl_4F molecule could

Fig.7. Calculated Equilibrium Constants for the Dissociation:

$PCl_4F \rightleftharpoons PCl_2F + Cl_2$.

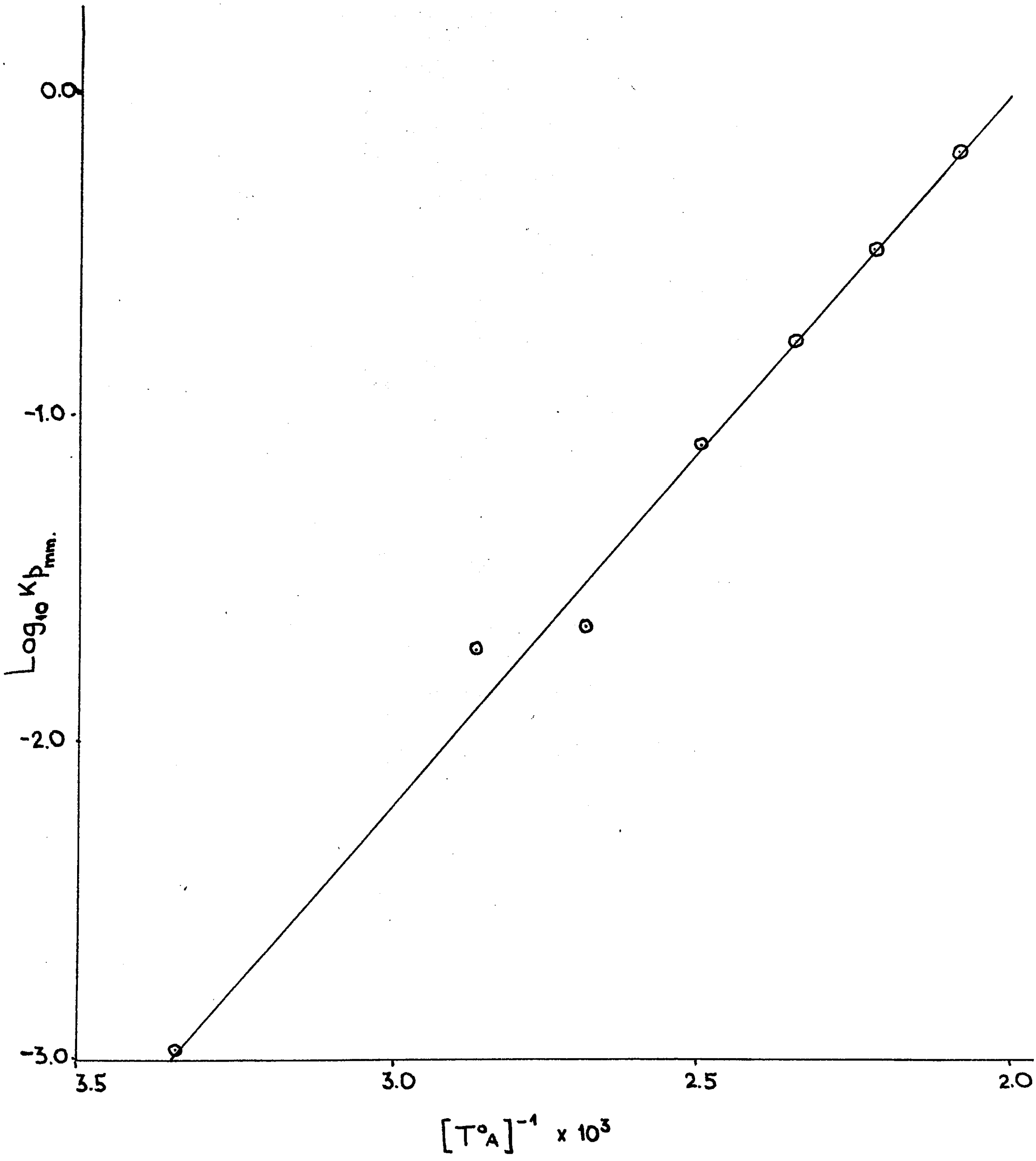


Table 12. Calculated Equilibrium Constants for the dissociation $PCl_4F \rightleftharpoons PCl_2F + Cl_2$.

$P_{PF_3Cl_2}$	$P_{obsvd.}$	P_{PF_5}	ΔP	$\log_{10}K_p$.	Temp.
124·0	124·3	62·0	0·3	-2·99	25
134·7	135·00	67·4	0·3	-3·23	50
144·9	146·10	72·5	1·2	-1·69	75
155·8	157·10	77·9	1·3	-1·65	100
166·1	168·80	83·1	2·7	-1·08	125
176·5	180·60	88·3	4·1	-0·73	150
187·7	192·50	93·9	4·8	-0·47	175
197·9	204·2	99·0	6·3	-0·17	200

be envisaged as either

$$PCl_4F \rightleftharpoons PCl_3 + ClF$$

or

$$PCl_4F \rightleftharpoons PCl_2F + Cl_2.$$

The second of these alternatives is to be preferred since the bond energy of a Cl-Cl bond (57·8 Kcals) is considerably less than a Cl-F bond (86·4 Kcals) (28). No experimental evidence is available, however, to support this. The system may be represented by the following scheme:

$$2PF_3Cl_2 \longrightarrow PF_5 + PCl_4F \rightleftharpoons PCl_2F + Cl_2.$$

By making use of the pressure increases observed which cause deviation from the Charles' Law line when disproportionation occurs, determination of the $\log_{10}K_p$ values can be carried out. The results are contained in table 12 and figure 7; a plot of $\log_{10}K_p$ versus T^{-1} shows a good linear relationship.

The straight line plot of $\log_{10}K_p$ against T^{-1} gives a value for $\Delta H_{(dissociation)}$ of 10·5 Kcals. This is to be compared with the corresponding value of 22 Kcals for phosphorus pentachloride. From these observations, it would appear that for a given temperature and pressure, the percentage dissociation is greater in phosphorus pentachloride than in PCl_4F.

These experiments did not provide any further information concerning the nature of the reaction which takes place on pyrolysis of PF_3Cl_2.

DETAILED EXAMINATION OF THE PYROLYSIS PRODUCTS.

EXAMINATION OF THE SOLID PRODUCTS.

The observations that a solid phase deposited on the apparatus walls suggested the next step in the study of the pyrolysis. Samples of pure PF_3Cl_2 were heated to a temperature of 220° for several days in specially designed glass bulbs. After allowing the system to cool, the volatile phase was pumped off and the solid phase examined.

Investigation of the solid phase was carried out under the following main headings:

a) X-ray powder diagram.

b) Analysis.

c) Detection of the $[PF_6^-]$ ion.

d) pH Titration.

e) I.R. Spectrum.

a) Powder diagram of solid phase.

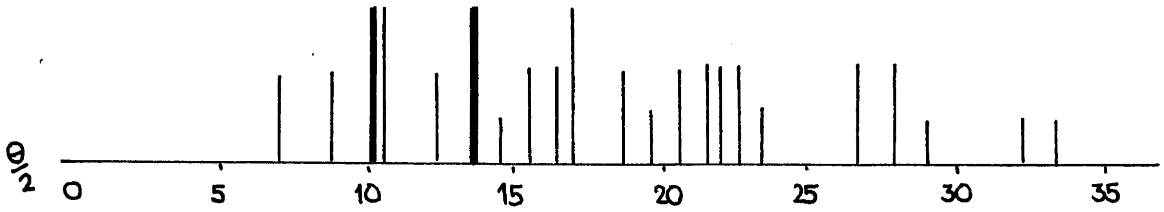
The powder diagram of the solid phase was measured and a scale reproduction is shown in figure 8. Also reproduced in the figure is the powder pattern of $[PCl_4^+][PF_6^-]$ and the published pattern of $[PCl_4^+]F^-$ (16). The values of $\theta/_2$ are compared in table 13.

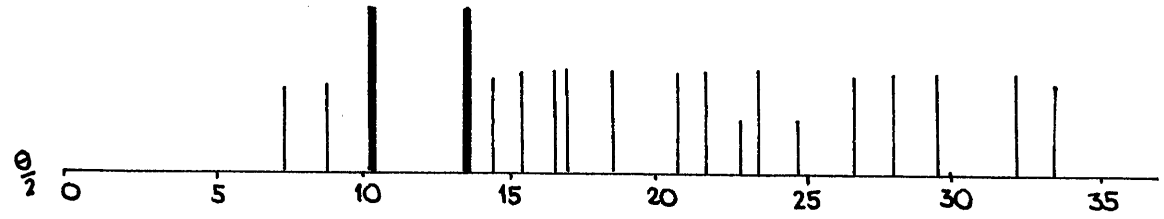
It is clear from figure 8, that the pattern of the solid obtained by pyrolysis is a superposition of the patterns of $[PCl_4^+][PF_6^-]$ and $[PCl_4^+]F^-$. The values of $\theta/_2$ in table 13 show good agreement and no value remains unaccounted for.

Table 13. X-ray powder data for the solid resulting from pyrolysis.

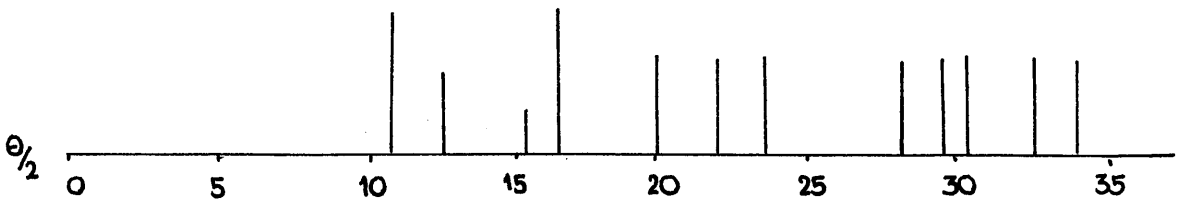
$\theta/2$	strength	$[PCl_4^+][PF_6^-]$	$[PCl_4^+]F^-$
7·35	m	7·8	
9·00	m	9·0	
10·44	vs	10·6	
10·80	s		10·8
12·69	m		12·5
13·80	vs	13·7	
14·80	w	14·6	
15·76	m	15·6	15·3
16·70	m	16·7	16·5
17·33	s	17·2	
19·00	m	19·0	
19·96	w		19·9
21·00	m	21·2	
21·75	m		21·9
22·26	m	22·3	
23·07	m	23·0	
23·70	w	23·7	23·4
27·15	m	27·1	
28·20	m	28·3	28·3
29·37	w		29·5
32·45	w	32·3	32·8
33·60	w	33·6	33·9

Fig.8. X-ray Powder Diagram of the Solid Resulting from Pyrolysis.





$[PCl_4^+][PF_6^-]$



$[PCl_4^+]F^-$

b) Analysis of the Solid.

The results of the analysis of the solid material were found to be dependent on the conditions under which hydrolysis of the solid took place. Thus, hydrolysis with dilute sodium hydroxide gave a phosphorus content approximately 66% of the value obtained by hydrolysis with boiling, concentrated nitric acid. This can be explained by the presence of the hexafluorophosphate ion, $[PF_6^-]$, detected by complex formation with Nitron, which is known to resist hydrolysis under mild conditions. Thus, in subsequent analyses of the solid, hydrolysis was conducted under the vigorous conditions cited above.

Analysis was carried out for phosphorus, (volumetrically) and chlorine (gravimetrically) whilst fluorine was obtained by difference. The results were:

Chlorine	% :	53·5, 53·8	Mean:	53·65
Phosphorus	% :	18·3, 18·3		18·3
Fluorine	% :	28·2, 27·9		28·05

The weight of solid sample taken was 0·1092g. comprised of 0·06452 g.atom phosphorus, 0·1649 g.atom chlorine and 0·1615g. atom fluorine. From these results, the atomic ratio of phosphorus to halogen was 1:5·01.

The overall analytical results are thus completely satisfactory. If, as it appears from X-ray evidence, the solid is a unique mixture of $[PCl_4^+]F^-$ and $[PCl_4^+][PF_6^-]$, then its percentage composition can be obtained from the results of the analysis. Thus the atomic ratio of chlorine to phosphorus was found to be 2·566:1 and from this the composition of the solid was 44·1% $[PCl_4^+]F^-$ and 55·9% $[PCl_4^+][PF_6^-]$.

c) Detection of the Hexafluorophosphate ion.

The ability of Nitron reagent (a mono acid base of formula diphenyl-endo-anilo-dihydrotriazole, $C_{20}H_{16}N_4$) to complex with a wide range of anions yielding sparingly soluble compounds is well known. Kolditz (15) has shown that Nitron will complex with the hexafluorophosphate ion.

Since the X-ray studies indicated the presence of $[PCl_4^+][PF_6^-]$ in the mixed solid material obtained by pyrolysis it should be possible to verify the existence of the $[PF_6^-]$ ion by complex formation with Nitron.

A sample of the solid material was hydrolysed with dilute alkali (under these conditions the $[PF_6^-]$ ion remains unchanged) and a complex was formed with Nitron. The melting point of this complex was 228° (Kolditz: 229°). The I.R. spectrum showed frequencies attributable to P-F bonding whilst the X-ray powder diagram gave a pattern identical with that of the compound formed by reacting Nitron with a pure sample of $[PCl_4^+][PF_6^-]$.

Details of the I.R. spectra and X-ray powder diagram of Nitron and the Nitron-$[PF_6^-]$ complex are given in the Appendix.

d) pH Titration of the Solid.

A sample of solid, shown by analysis to have the composition 44% $[PCl_4^+]F^-$ and 56% $[PCl_4^+][PF_6^-]$, was hydrolysed under acid conditions and the hydrolysate titrated against standard sodium hydroxide, the pH value being noted after each addition of titrant. The results are set out in table 14 and figure 9.

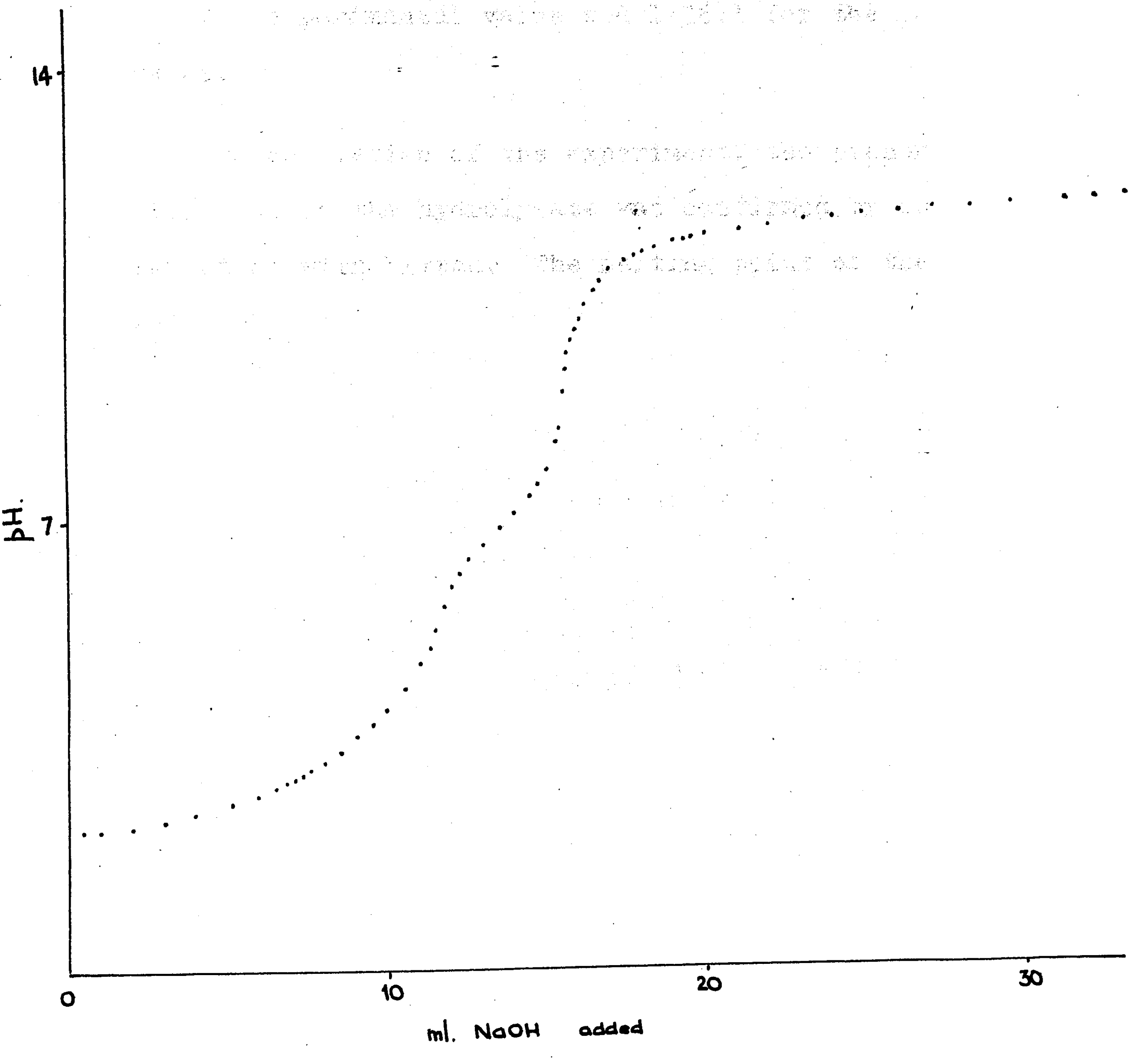
The titration curve in figure 9 shows a marked inflexion at pH 5 and pH 9. Using the analytical data, there are found to be 4·0 equivalents of HCl, 0·56 equivalents of HPF_6 and 1·0 equivalents of H_3PO_4 (first ionisation); this gives an equivalent weight of the solid at pH 5 of 45·4. At pH 9, in addition to the 5·56 equivalents at pH 5, there are 0·44 equivalents of HF and 1·0 equivalents of H_3PO_4 (second ionisation); thus at pH 9, an equivalent weight for the solid material of 36·1 was deduced. In this titration it is assumed that HF would behave as a weak acid.

The experimental value of the equivalent weight at pH 9 was found to be 43·5. This value is of the correct magnitude and thus supports the interpretation made of the

Table 14. pH Titration of the Solid.

ml NaOH	pH	ml NaOH	pH	ml NaOH	pH
0·0	2·16	11·75	5·65	17·5	10·95
0·5	2·20	12·0	5·92	17·8	11·05
1·0	2·23	12·25	6·18	18·0	11·07
2·0	2·29	12·50	6·35	18·5	11·15
3·0	2·38	13·0	6·62	18·75	11·19
4·0	2·49	13·5	6·86	19·0	11·25
5·0	2·61	14·0	7·07	19·25	11·28
6·0	2·75	14·5	7·35	19·50	11·31
6·5	2·85	14·75	7·52	20·0	11·36
6·75	2·91	15·0	7·73	21·2	11·45
7·0	2·99	15·25	8·10	22·0	11·50
7·25	3·07	15·4	8·42	23·1	11·57
7·50	3·12	15·5	8·90	24·0	11·61
8·0	3·29	15·6	9·30	25·0	11·68
8·5	3·45	15·7	9·52	25·0	11·70
9·0	3·64	15·8	9·75	27·0	11·75
9·5	3·84	15·9	9·93	28·0	11·78
10·0	4·06	16·0	10·05	29·5	11·81
10·5	4·32	16·25	10·32	31·1	11·86
11·0	4·74	16·5	10·51	32·0	11·89
11·25	5·03	16·75	10·65	33·0	11·95
11·50	5·28	17·0	10·79	38·0	12·0

Fig. 9. pH Titration of Solid.



inflexions in the titration curve. Considerable error may occur in the absolute value through the presence of hydrofluoric acid.

The ratio of the titres at pH 9 and at pH 5 also show reasonable agreement between the experimental and calculated values; the ratios were found to be 1·26:1 for the experimental value and 1·36:1 for the calculated value.

On completion of the experiment, the presence of the $[PF_6^-]$ ion in the hydrolysate was confirmed by complex formation with Nitron. The melting point of the complex was 228°.

e) I.R. Spectrum of the Solid.

The detailed spectrum of the mixed solid phase measured as a mull, is as follows:

405m, 460m, 485m,
465s, 575s, 660s,
675s, 735s, 785s,
830-888 (shoulder) cm.$^{-1}$

It was not possible to allocate these frequencies with any certainty because of the difficulty experienced in obtaining reference spectra. By comparison with the spectrum of the $[PF_6^-]$ ion however, the shoulder 830-888 cm.$^{-1}$ can be allocated to P-F stretching.

The spectrum of the vapour phase in equilibrium with the solid at 20° was also measured. The detailed spectrum is:

800m, 816m, 820m,
830m, 890m, 900s,
930s, cm.$^{-1}$

DETAILED EXAMINATION OF THE VOLATILE PHASE.

The examination of the volatile phase obtained by pyrolysis, was carried out under three main headings:

a) Examination of I.R. spectra.

b) Analysis and vapour density measurement.

c) Measurement of mass spectra.

a) I.R. spectra of the vapour phase.

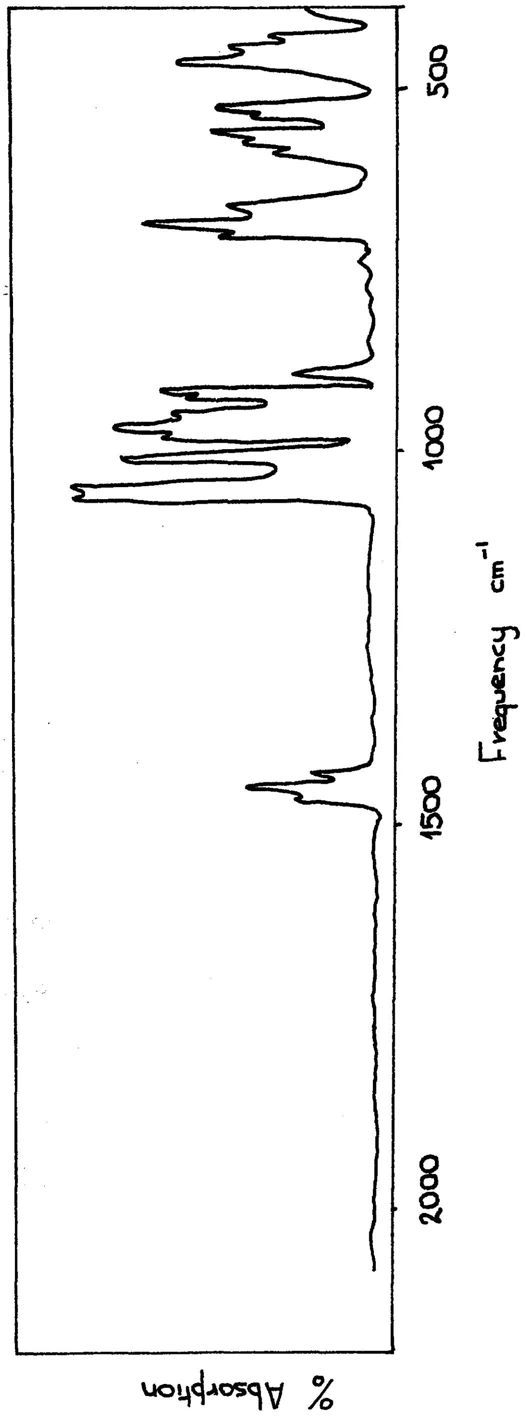
The details of the I.R. spectrum of the vapour phase are as follows:

395m, 430w, 466w,
472w, 490m, 528m,
535s, 542s, 565s,
575m, 590m, 635m,
675s, 680s, 692m,
700m, 798m, 868s,
875s, 888m, 900s,
908s, 935s, 940s,
950s, 960s, 999s,
1020s, 1032s, 1320w,
1365w, 1410m, 1425m,
1430m. cm.$^{-1}$

- the spectrum is reproduced in figure 10.

A partial resolution of the volatile phase was effected by fractional distillation. Two fractions were obtained, fraction I condensing at -96° whilst fraction II condensed at -180°. Further fractionation of fraction I

Fig. 10. The I.R. Spectrum of the Vapour Phase.



did not result in any additional separation. The details of the separation in the range 670 to 2000 wave numbers is as follows:

Fraction I	794s,	820s,	830s,
	890s,	905s,	938s,
	950s,	960s,	995s,
	1032s,	1024s,	1326m,
	1327m,	1353m,	1410m,
	1425m,	1430m.	
Fraction II	875m,	999s,	1024s,
	1410m,	1425m,	1430m,

The I.R. spectra of phosphorus oxyfluoride, phosphorus pentafluoride, phosphorus trifluoride, silicon tetrafluoride and PF_3Cl_2 were used as references and are to be found in the Appendix.

Using the reference spectra for comparison purposes, the presence of silicon tetrafluoride, phosphorus oxyfluoride, phosphorus pentafluoride, and PF_3Cl_2 were unambiguously detected in the vapour phase formed after pyrolysis. The fractionation process resulted in the separation of phosphorus oxyfluoride and silicon tetrafluoride as fraction II; this was verified by a molecular weight measurement (Found: 104, Required M.W. for SiF_4, POF_3 : 104).

Allocation of frequencies in the spectrum of the volatile phase by reference to the spectra of known compounds did not, however, account for all the frequencies found. Thus frequencies at

466w, 528m, 542s,
798s, 830s, 888m, $cm.^{-1}$

remained unallocated. However, comparison of these unallocated frequencies with the I.R. spectrum of the vapour phase in equilibrium with the mixed solid obtained by pyrolysis showed important similarities. Furthermore, the vapour phase in equilibrium with solid $[PCl_4^+][PF_6^-]$ at 40° can be shown by its I.R. spectrum to be PF_3Cl_2. This observation leaves frequencies at 800, 830, and 890 $cm.^{-1}$ unallocated in the spectrum of the solid $\rightleftharpoons$ vapour system. These frequencies are presumably due to the vapour phase in equilibrium with $[PCl_4^+]F^-$ and are very similar to those unallocated frequencies occuring in the spectrum of the volatime products of pyrolysis of PF_3Cl_2. These observations make it seem very likely that these new frequencies are due to the vapour phase in equilibrium with $[PCl_4^+]F^-$, presumably PCl_4F. Further proof of the existence of the species PCl_4F in the vapour phase is furnished by the mass spectra measurements and the good agreement obtained in the analytical results from the vapour phase products if PCl_4F is assumed to be present.

b) Analysis of the vapour phase.

A known amount of volatile material was hydrolysed with dilute sodium hydroxide; the hydrolysate was analysed for phosphorus and chlorine. The result of the analysis was: -

Chlorine	%	25·2	24·8	Mean	25·0
Phosphorus	%	18·9	18·8		18·9

Ratio chlorine : phosphorus = 1·16:1

Measurement of the molecular weight of the vapour phase gave a value of 125·8.

The I.R. spectrum shows the presence of phosphorus oxyfluoride and silicon tetrafluoride, formed by attack of phosphorus pentafluoride on the glass which may be represented by the equation:

$$PF_5 \xrightarrow{SiO_2} POF_3 + 0{\cdot}5SiF_4.$$

If all the phosphorus pentafluoride attacks the glass in this way, then the average molecular weight would be 124·2. This value indicates that not all the phosphorus pentafluoride has so reacted but that some remains as such in the vapour mixture. (This conclusion is supported by the I.R. evidence).

The experimental molecular weight value of 125•8 can be accounted for by a vapour mixture with the following composition:

9•1% PF_5, 22•8% PCl_4F, 22•8% SiF_4, 45•6% POF_3.

This composition requires the ratio of chlorine:phosphorus to be 1•17:1 (found 1•16:1). This calculated composition of the gaseous mixture as shown above shows good agreement with the analytical results and the molecular weight determination.

By making use of the measured pressure reduction which resulted from pyrolysis a method of checking the composition of the solid phase which is also formed, is available.

It was found, initially, that there was a pressure of 400 mm. of pure PF_3Cl_2 in the pyrolysis apparatus of volume 48•0 ml., after pyrolysis the residual pressure was 215•7 mm.

Thus, initially present : $1{\cdot}05 \times 10^{-3}$ g.mole. PF_3Cl_2

finally present : $0{\cdot}566 \times 10^{-3}$ g.mole. PF_3Cl_2

The residue was comprised of: $0{\cdot}258 \times 10^{-3}$ g.mole. POF_3
$0{\cdot}129 \times 10^{-3}$ g.mole. SiF_4
$0{\cdot}129 \times 10^{-3}$ g.mole. PCl_4F
$0{\cdot}051 \times 10^{-3}$ g.mole. PF_5

Now if no attack by phosphorus pentafluoride on the glass had occurred then there would have been:

$0{\cdot}309 \times 10^{-3}$ g.mole. PF_5

and the solid phase would thus be comprised of:

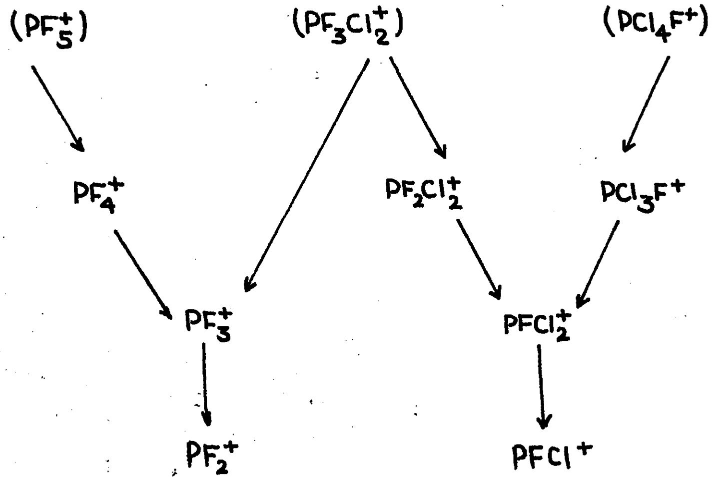
$0{\cdot}180 \times 10^{-3}$ g.mole. $[PCl_4^+]F^-$
and $0{\cdot}216 \times 10^{-3}$ g.mole. $[PCl_4^+][PF_6^-]$

i.e. the composition of the mixed solid from this calculation is 44·1% $[PCl_4^+]F^-$ and 55·9% $[PCl_4^+][PF_6^-]$.
This result is identical with the independent analytical results of the solid phase.

The interpretation of the analytical results from the volatile products of pyrolysis is therefore completely satisfactory.

c) The Mass Spectrum of the vapour phase.

The details of the mass spectrum of the vapour phase are set out in table 15. The mass peaks can be interpreted according to the scheme:



This scheme provides evidence for the presence of PCl_4F and PF_3Cl_2 in the vapour phase. Attack by phosphorus pentafluoride on the glass at the elevated temperature of pyrolysis explains the presence of SiF_4^+, POF_3^+ and POF_2^+.

Table 15. Mass Spectrum of Vapour Phase.

Mass	Assign.	Rqud.	Mass	Assign.	Rqud.
35	Cl^+	35		$POClF_2^+$	124
37	Cl^+	37	123	PF_3Cl^+	123
69	PF_2^+	69	125	PF_3Cl^+	125
85	$PClF_2^+$	85	136	PCl_3^+	136
87	$PClF^+$	87	138	PCl_3^+	138
	POF_2^+	85	140	PCl_3^+	140
88	PF_3^+	88		$POCl_2F^+$	136
101	PCl_2^+	101		$POCl_2F^+$	138
103	PCl_2^+	103		$POCl_2F^+$	140
104	SiF_4^+	104	139	$PF_2Cl_2^+$	139
	POF_3^+	104	141	$PF_2Cl_2^+$	141
107	PF_4^+	107	143	$PF_2Cl_2^+$	143
117	$POCl_2^+$	117	151	$PFCl_3^+$	155
119	$POCl_2^+$	119	153	$PFCl_3^+$	157
121	$POCl_2^+$	121	155	$PFCl_3^+$	159
120	$PFCl_2^+$	120	157	$PFCl_3^+$	161
122	$PFCl_2^+$	122		$POCl_3^+$	152
124	$PFCl_2^+$	124		$POCl_3^+$	154
	$POClF_2^+$	120		$POCl_3^+$	156
	$POClF_2^+$	122		$POCl_3^+$	158

The action of PF_3Cl_2 on glass at high temperatures is not known but mass peaks could be alotted to $POCl_2F^+$ $POClF_2^+$, $POCl_2^+$ and POF_2^+ which might be derived from the products of such a reaction. It is interesting in this connection to compare the energy requirements when a P-F or a P-Cl bond attacks a Si-O bond (28) thus:

	2 Si-O	2 P-F	2 Si-F	P=O
K.cals:	2 x 104	2 x 117	2 x 131	130

$$\Delta E = 150 \text{ K.cals.}$$

	2 Si-O	2 P-Cl	2 Si-Cl	P=O
K.cals:	2 x 104	2 x 78	2 x 87	130

$$\Delta E = 68 \text{ K.cals.}$$

Thus from thermodynamic considerations, it would appear that phosphorus pentafluoride would attack glass much more readily than PF_3Cl_2 and furthermore, in PF_3Cl_2, the P-F bond would react rather than the P-Cl bond. The position is complicated by the fact that attack on glass which has been previously baked out, does not appear to begin until temperatures of $> 140°$ are reached; and under these conditions PF_3Cl_2 tends to be unstable.

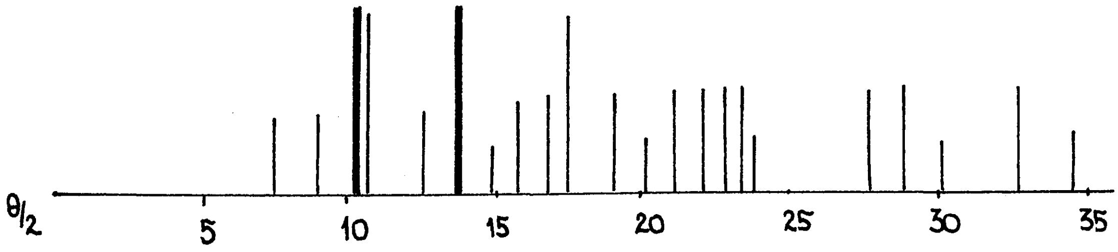
In the table of results, it will be seen that $POCl_3^+$, and PCl_3F^+ are given as alternative assignments for the mass peaks, 151, 153, 155, 157. The $POCl_3^+$ ion might conceivably have been formed by traces of moisture, released at the high temperature of the pyrolysis, reacting with the species PCl_4F. Associated with this is the ion formed by loss of a chlorine atom, namely $POCl_2^+$; however, alternatively this could also be formed from the $POCl_2F^+$ ion by loss of a fluorine atom.

The assignment of certain peaks is not completely unambiguous more particularly with regard to the oxy-compounds. The real value of the experiment lies in the supporting evidence it provides for the existence of phosphorus pentafluoride, PF_3Cl_2 and PCl_4F as constituents of the mixed vapour phase.

THE EXPERIMENTAL STUDY OF THE STABILITY OF PF_3Cl_2 AT ROOM TEMPERATURE.

Several samples of pure PF_3Cl_2 were sealed up in glass bulbs which had previously been flamed out under vacuum. The bulbs were stored in darkness at room temperature for several days. On examination, it was found that a white solid material had deposited on the walls of the apparatus. In addition, it was observed that the time during which the samples could be stored unchanged was dependent on the extent to which the storage vessels had been flamed out. The white solid material was investigated by studying its X-ray powder pattern, the results of which are found in table 16 and figure 11. Comparison of the powder lines with those of the reference compounds $[PCl_4^+][PF_6^-]$ and $[PCl_4^+]F^-$ showed the solid material to be exclusively a mixture of the two. Analysis of the solid phase for phosphorus, chlorine and fluorine

Fig.11 The X-ray Powder Diagram of the Solid obtained by Storage of PF_3Cl_2.



(by difference) gave the results:

Phosphorus %	:	19·0, 19·2	Mean:	19·1
Chlorine %	:	48·0, 48·8		48·4
Fluorine %	:	33·0, 32·0		32·5

These results give the composition of the solid as 86% $[PCl_4^+][PF_6^-]$ and 14% $[PCl_4^+]F^-$. Comparing these figures with the results from the investigation of the pyrolysis of PF_3Cl_2, it is seen that the solid phase, although comprised of the same constituents, has a higher $[PCl_4^+][PF_6^-]$ content when obtained by storage.

The variation of pressure with time of a stored sample was investigated as follows:

In an apparatus very similar to that used in the pyrolysis studies pressure measurements at room temperature were taken at suitable time intervals and then corrected to 20°. The results are given in table 17 and figure 12. After 35 days storage, the pressure of the system had fallen to 52% of the initial value. The plot of pressure versus time can be described by a straight line, as in figure 12, the reaction taking place having

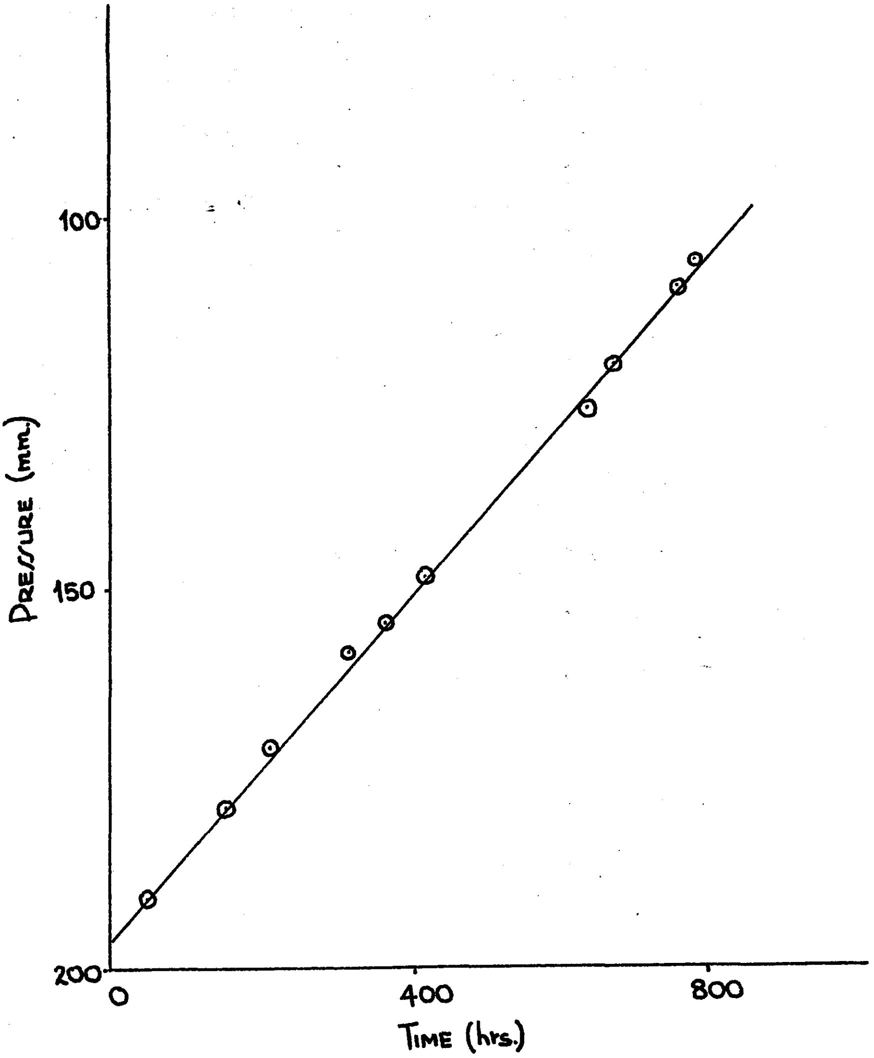
Table 16. X-ray powder photograph of the white solid obtained by storage of PF_3Cl_2.

$\theta/2$	Strength	$[PCl_4^+][PF_6^-]$	$[PCl_4^+]F^-$
7·40	m	7·8	
9·08	m	9·0	
10·45	vs	10·6	
10·76	s		10·8
12·70	w		12·5
13·75	vs	13·7	
14·80	w	14·6	
15·71	m	15·6	15·3
16·73	m	16·7	16·5
17·34	s	17·2	
19·00	m	19·0	
19·98	w		19·9
21·11	m	21·2	
21·88	w		21·9
22·63	m	22·3	
23·23	m	23·0	
23·85	w	23·7	23·4
24·85	m	25·0	
27·28	m	27·1	
28·98	w	28·3	28·3
33·60	w	33·6	33·9

Table 17. Stability of PF_3Cl_2 at 20°

Press. mm.	Time hrs.	Press mm.	Time hrs.
195·92	0	171·80	201·5
195·87	9·5	162·60	262·5
193·77	21·5	159·10	290·8
193·20	28·5	159·30	310·5
192·00	47·0	157·10	333·5
189·67	55·0	155·10	364·5
185·69	93·5	150·60	502·5
184·02	101·5	135·60	598·5
182·40	117·5	126·00	648·5
180·86	129·5	119·60	679·0
179·10	142·5	117·11	719·3
178·22	149·0	113·73	733·3
176·30	166·0	108·90	790·5
174·80	174·3	106·41	818·8
172·70	190·0	102·51	845·3

Fig 12. The Stability of PF_3Cl_2 at Room Temperature.



zero order kinetics. The gradient of the line gives a value of 0·12 $mm.hrs^{-1}$ for the rate constant k. The observation that zero order kinetics hold indicates that the reaction which occurs is initiated catalytically on the glass surface of the apparatus. In addition, zero-order kinetics implies that the catalytic surface is almost completely covered by the reacting molecules so that the number of molecules in a condition to react is constant; in other words, the capacity of the glass surface is insufficient to deal with all the molecules at once.

Mention has been made above, of the dependence of the rate of reaction on the efficiency with which the glass apparatus is baked out. From these considerations then it seems reasonable to postulate that the reaction which occurs when PF_3Cl_2 is allowed to stand at room temperature, is in some way connected with traces of water adsorbed on the glass surfaces of the apparatus.

The residual volatile phase, after the pressure of the system had fallen to 52% of the initial value, was separated from the solid phase and its I.R. spectrum measured. The details obtained at 5 mm. pressure are as follows:

395m, 465m, 472m,
485m, 490m, 528s,
535s, 545s, 565s,
575s, 590m, 630s,
670s, 675m, 830s,
868m, 875s, 888s,
900s, 908s, 940s,
950s, 960s, 999s,
1024s, 1031s, 1355m,
1365m, 1405m, 1420m,
1430m. $cm.^{-1}$

These frequencies are almost identical with those obtained from the spectrum of the volatile phase which is formed by pyrolysis. Thus comparison with the reference spectra given in the Appendix indicates the presence of POF_3, SiF_4, PF_5, PF_3Cl_2, and probably PCl_4F. The frequencies at 1355 and 1365 $cm.^{-1}$ are interesting since they are intermediate between the P-O stretching frequency in POF_3 (1415, 1430 $cm.^{-1}$) and $POCl_3$ (1280 $cm.^{-1}$). These intermediate frequencies may thus represent mixed phosphorus chloro-fluoro oxyhalides, some evidence of which is provided by the mass spectrometer work. However, no definite conclusions can be reached in this respect without further experimental evidence.

The most important factor which emerges from the study of the effect of storage at room temperature on PF_3Cl_2, is the striking similarity between the products of reaction obtained and those resulting from the pyrolysis study. A significant factor is the much greater proportion of $[PCl_4^+][PF_6^-]$ relative to $[PCl_4^+]F^-$ which is obtained from the storage experiment.

DISCUSSION OF THE POSSIBLE MECHANISM FOR THE REACTION

$$2PF_3Cl_2 \longrightarrow PF_5 + PCl_4F.$$

The disproportionation of PF_3Cl_2 yielding PCl_4F and phosphorus pentafluoride has been shown to occur under two sets of conditions: by the action of heat at above 150° or by prolonged storage at room temperature.

Considering the reaction, in general terms, there are two possible modes of action, either by an ionic or a molecular path.

Kolditz (21) has discussed the formation of $[PCl_4^+]F^-$ from PCl_4F in the light of Siebert's work (29) which considered the formation of the ionic from the molecular form of phosphorus pentachloride. The principal tenet of this theory is that in phosphorus pentahalide molecules which adopt the trigonal bipyramidal configuration, the apical bonds are considered to be the reactive sites at which ionisation can occur. Thus in the case of PCl_4F, Kolditz suggests that the fluorine atom, initially located in a planar position migrates to the apical position and thence splits off. In PF_3Cl_2, the fluorine atoms are known to occupy the planar positions. Thus, a similar procedure to form $[PCl_4^+][PF_6^-]$ is not envisaged as being likely since the degree of fluorine atom switching would require a large activation energy. These conclusions have been substantiated by the experimental results of this present study: formation of $[PCl_4^+][PF_6^-]$ results from combination of PCl_4F or $[PCl_4^+]F^-$ and phosphorus pentafluoride.

A simple ionisation process could be envisaged in the following manner:

$$PF_3Cl_2 \rightleftharpoons [PF_2Cl_2^+] + F^-$$

$$\text{or} \quad PF_3Cl_2 \rightleftharpoons [PF_3Cl^+] + Cl^-$$

Subsequent reaction between the cationic species and molecular PF_3Cl_2, would then lead to formation of phosphorus pentafluoride and, after various interchanges, PCl_4F. Reaction between the anions and PF_3Cl_2 could lead to formation of a range of intermediate ions from which PCl_4F and phosphorus pentafluoride might eventually be obtained.

By a process of chlorine switching, either singly or doubly, the ions $[PF_2Cl_2^+]$ or $[PF_3Cl^+]$ may lead to the required products. For example, the double chlorine switch can be illustrated in the following manner:

$$[PF_2Cl_2^+] + PF_3Cl_2 \longrightarrow [PCl_4^+] + PF_5.$$
$$\longrightarrow [PF_4^+] + PCl_4F$$

$$[PF_3Cl^+] + PF_3Cl_2 \longrightarrow [PCl_3F^+] + PF_5$$
$$\longrightarrow [PF_4^+] + PCl_4F.$$

- the ions formed in this way could then react with Cl^- or F^-.

The routes by which phosphorus pentafluoride and PCl_4F might be obtained from ionic intermediates are very varied. Consequently, only a brief outline of the possible reaction paths has been considered above.

The possibility of the disproportionation reaction being catalysed by hydrogen halide formation has already been mentioned. A displacement type process with hydrogen chloride or fluoride reacting with PF_3Cl_2 to displace fluorine or chlorine could produce the required products. The possibility of formation of compounds of the type HPF_4Cl_2 or HPF_3Cl_3 from reaction between PF_3Cl_2 and hydrogen halide cannot be ignored.

With regard to a molecular mechanism, the possibility of a dissociation reaction must first be discussed. The possible dissociation scheme might be as follows:

$$\begin{aligned} PF_3Cl_2 &\rightleftharpoons PF_3 + Cl_2 \\ &\rightleftharpoons PF_2Cl + FCl \\ &\rightleftharpoons PFCl_2 + F_2 \end{aligned}$$

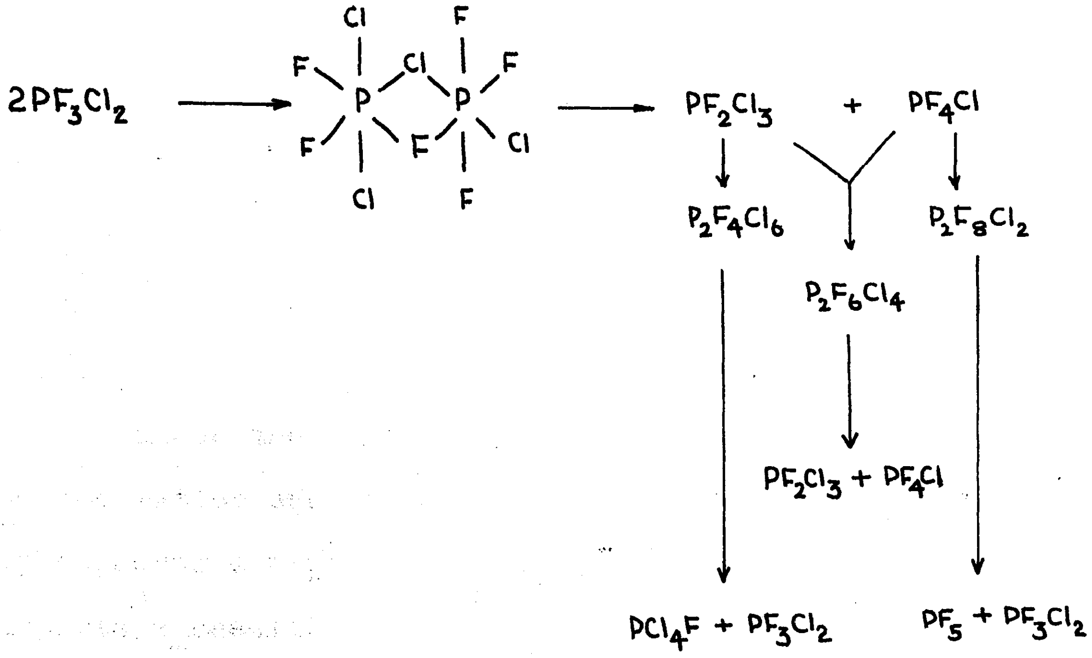
The required reaction products could then be formed as follows:

$$PCl_2F + Cl_2 \longrightarrow PCl_4F$$

$$PF_3 + F_2 \longrightarrow PF_5$$

However, no evidence has ever been obtained in this work as to the occurrence of dissociation of the PF_3Cl_2 molecule. Certainly, if such a process occurred to any extent, the dissociation products should be detectable by measurement of I.R. spectra. Moreover the dissociated systems might be expected to recombine to a more varied extent than is required to produce PCl_4F and phosphorus pentafluoride.

Evidence of the existence of units containing two phosphorus atoms has been obtained from mass spectra studies of the vapour phases of $[PCl_4^+][PCl_5F^-]$ and phosphorus pentachloride. It is likely that such biphosphorus units occur with PF_3Cl_2 vapour. Molecular rearrangement processes involving vapour phase association of trigonal bipyramidal molecules might proceed as follows:



As can be seen from this scheme, the required products are formed together with PF_2Cl_3 and PF_4Cl although, as already mentioned, no evidence of these compounds has ever been obtained. The conception of a mixed chlorine-fluorine bridge occurring in the biphosphorus unit is rather difficult to accept by comparisons with other compounds. The formation of such a bridge is, however, essential if the required products are to be obtained. The likely occurrence of biphosphorus containing units does make it seem possible that the reaction mechanism is of a molecular type.

No definite conclusions can be drawn as to the actual mechanism involved without a specific experimental study. Both molecular and ionic paths are equally favoured, and in many cases the polarity of the bonds make the former and the latter equivalent. Evidence of the existence of biphosphorus containing units in phosphorus pentahalides supports a reaction occurring by means of a molecular mechanism; the lability of ligands in phosphorus chemistry is well known and favours the idea of a chlorine-switching process.

Further experimental study might well be directed along the following lines. The preparation of compounds containing the $[PF_2Cl_2^+]$ ion would be important as their reaction with PF_3Cl_2 could then be studied. A more detailed search for the presence of small amounts of 'by-products' such as PCl_3F_2, and PF_4Cl would also be necessary. Use of labelled phosphorus trifluoride and chlorine would show whether these compounds were intermediates in the reaction, as suggested in the discussion of the molecular dissociation process.

PART II

THE PYROLYSIS OF $[PCl_4^+][PF_6^-]$.

INTRODUCTION.

The solid ionic compound $[PCl_4^+][PF_6^-]$ is of particular interest in relation to the study of the molecular compound PF_3Cl_2. In the preceding investigation of the stability of PF_3Cl_2 under varying conditions, $[PCl_4^+][PF_6^-]$ has consistently occurred as a product of reaction. It was thus natural to study the stability of $[PCl_4^+][PF_6^-]$ to obtain some information with regard to its relationship with PF_3Cl_2.

Attention was primarily focused on the action of heat on $[PCl_4^+][PF_6^-]$ under conditions similar to those used in the pyrolysis study of PF_3Cl_2.

Kolditz has reported the pyrolysis of $[PCl_4^+][PF_6^-]$ in arsenic trichloride suspension as leading to the formation of $[PCl_4^+]F^-$. This compound is initially contaminated with $[PCl_4^+][PF_6^-]$ which can be removed by sublimation. The formation of liquid PCl_4F by distillation of a $[PCl_4^+][PF_6^-]$ -arsenic trichloride mixture is also reported in this paper. The compound PCl_4F, in either the molecular or ionic forms was of particular interest and importance to the PF_3Cl_2 study and thus the work of Kolditz was repeated with the preparation of this compound in view.

VAPOUR PHASE STUDY OF THE PYROLYSIS OF $[PCl_4^+][PF_6^-]$.

The pressure of a known value and mass of $[PCl_4^+][PF_6^-]$ vapour was measured over a range of temperature by a static method; the apparatus for this experiment was very similar to that used in the PF_3Cl_2 pyrolysis studies. The results of this determination are set out in table 18 and plotted in figure 13. From the graph, it is seen that a linear relationship between pressure and temperature holds above 100°, and thus no solid material remains above this temperature. There is a deviation from the Charles' Law line above 150°, the observed pressures being larger than those required for the theoretical line. The temperature was raised to ca.250° and then lowered to ca.100° and then raised again to ca.170°. This portion of the graph is described (for both ascending and descending temperatures) by a straight line whose slope is greater than the Charles' Law line. It is possible to calculate the molecular weight of the vapour at any temperature between 100° and 250°. This was done for several temperatures and the results obtained are shown in table 19. The molecular weight values calculated for

Table 18. Action of Heat on $[PCl_4^+][PF_6^-]$.

Temp °C	Pressure mm.
98·8	78·92
122·8	84·17
150·0	91·77
171·3	100·22
194·5	107·18
218·0	116·29
224·0	125·32
229·0	123·33
206·5	116·00
186·5	109·97
155·0	100·01
125·0	91·00
93·5	81·77
143·0	95·70
168·9	103·41
115·0	88·60

Fig.13. The Pyrolysis of $[PCl_4^+][PF_6^-]$.

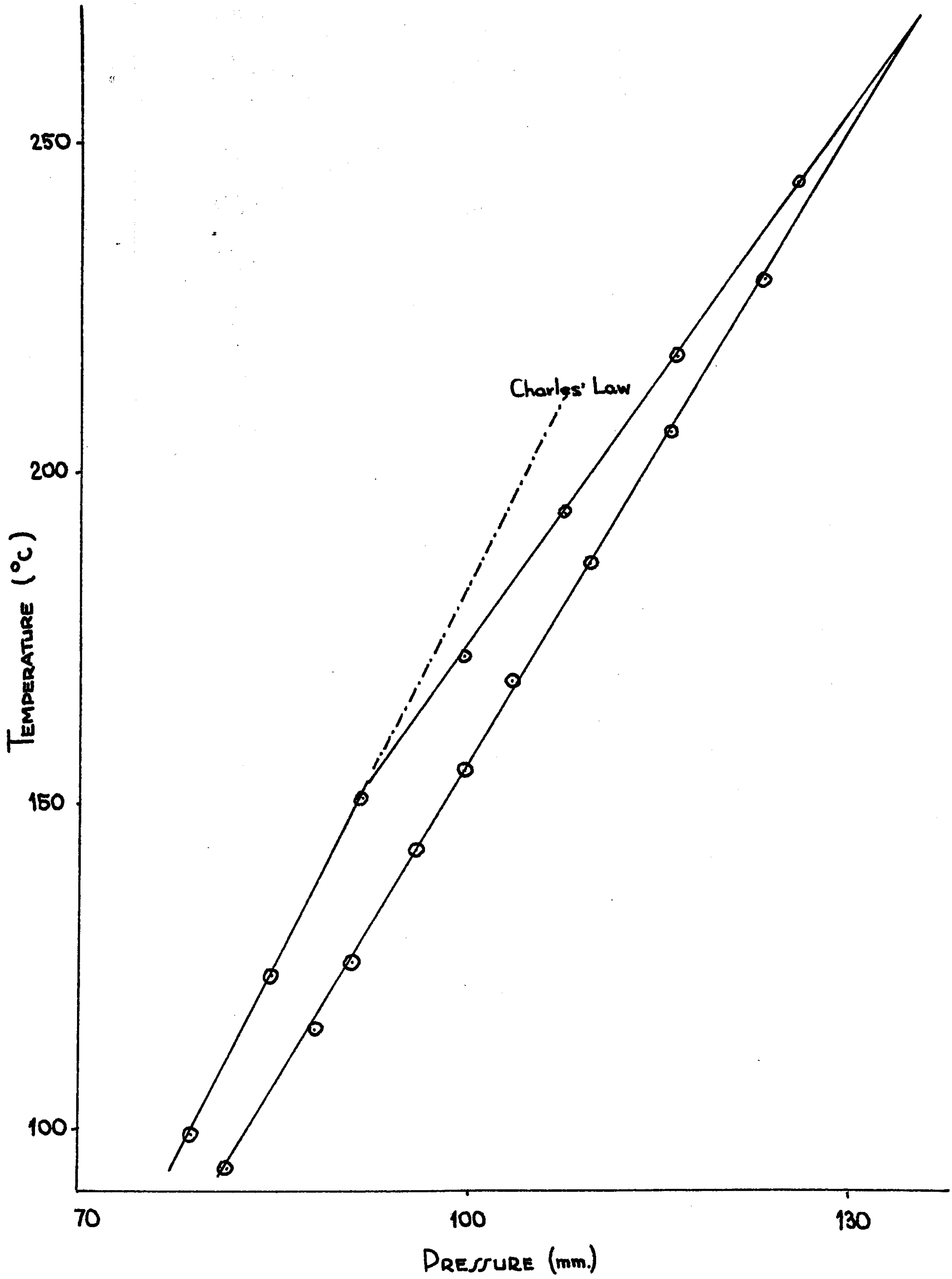


Table 19. Molecular Weight of $[PCl_4^+][PF_6^-]$ vapour.

Temp °C	Observed M.W. (Theor=317·8)
98·8	160·7
122·8	160·6
150·0	157·8
171·3	151·5
194·5	148·9
219·0	144·5
244·0	140·9
229·0	139·0
206·5	141·9
186·6	142·7
155·0	146·2
125·0	149·4
93·5	153·5
143·0	148·5
168·9	146·0
115·0	149·6

the experimental points which lie on the Charles' Law line, are in the range 159±1·5. These values are in keeping with a gaseous phase which is either PF_3Cl_2 or an equimolar mixture of PCl_4F and phosphorus pentafluoride. In view of the reproducibility of the Charles' Law line in the case of PF_3Cl_2 (page 57) the gaseous phase cannot be a mixture of PCl_4F and phosphorus pentafluoride since this would result in formation of $[PCl_4^+]F^-$ and $[PCl_4^+][PF_6^-]$ on cooling below ca.75° and thus cause deviation from the Charles' Law line. Furthermore, it has been shown from studies of I.R. spectra, that the vapour phase in equilibrium with $[PCl_4^+][PF_6^-]$ up to 40° is PF_3Cl_2; no evidence for PCl_4F or phosphorus pentafluoride was found. From these observations, it is clear that the molecular weight values of 159±1·5 describe a gaseous phase at $<$ 140° consisting of PF_3Cl_2 rather than PCl_4F and phosphorus pentafluoride.

The pattern of variation of pressure with temperature in this system is very similar to that exhibited in the pyrolysis study of PF_3Cl_2. Both systems initially obey Charles' Law up to ca.150°, thereafter deviation occurs due to observed pressures being higher than required for the theoretical line. After this transition period, the behaviour of both systems can be described by a straight line whose slope is greater than the initial Charles' Law line.

I.R. SPECTRUM OF VOLATILE PRODUCTS OF PYROLYSIS OF $[PCl_4^+][PF_6^-]$.

The details of the I.R. spectrum measured at 10 mm. pressure, of the volatile phase produced by pyrolysis are as follows:

395m, 460m, 473s,
482s, 490m, 508m,
523w, 535w, 565m,
628s, 670m, 675m,
798m, 835s, 865m,
870s, 892s, 900s,
908s, 940s, 950s,
960s, 999s, 1024s,
1032s, 1360m, 1405m,
1420m, 1430m. $cm.^{-1}$

These observed frequencies are very similar to the spectrum obtained from the volatile phase resulting from the pyrolysis of PF_3Cl_2. The presence of SiF_4, POF_3, PF_5, PF_3Cl_2 and probably PCl_4F is shown by comparing the experimental result with reference spectra of the individual constituents.

The most striking conclusion which can be drawn from this study of $[PCl_4^+][PF_6^-]$ is the close similarity in the behaviour of $[PCl_4^+][PF_6^-]$ and PF_3Cl_2 when heated. Thus when $[PCl_4^+][PF_6^-]$ is heated the initial reaction is the formation of the vapour phase consisting of PF_3Cl_2, which then undergoes pyrolysis as described previously.

PYROLYSIS OF $[PCl_4^+][PF_6^-]$ IN A SOLVENT.

The pyrolysis of $[PCl_4^+][PF_6^-]$ for 3-4 hours in arsenic trichloride as solvent was reported by Kolditz to lead to the formation of $[PCl_4^+]F^-$ together with the evolution of phosphorus pentafluoride and PF_3Cl_2 as gaseous products. The $[PCl_4^+]F^-$ obtained was contaminated with $[PCl_4^+][PF_6^-]$ which could be effectively removed by sublimation at 80° and 1 mm. pressure for fifteen minutes (16).

It was with a view to repeating this preparation of $[PCl_4^+]F^-$ that a pyrolysis of $[PCl_4^+][PF_6^-]$ in arsenic trichloride was carried out. The solid product obtained was a mixture of $[PCl_4^+][PF_6^-]$ and $[PCl_4^+]F^-$, verified by an X-ray powder photograph; the X-ray results are set out in table 20, from which it is seen that three lines are obtained which do not belong either to $[PCl_4^+][PF_6^-]$ or $[PCl_4^+]F^-$. A chlorine analysis should provide a good method of assessing the amount of $[PCl_4^+]F^-$ present since this latter substance has a chlorine content of 74·0% compared with 44·6% for $[PCl_4^+][PF_6^-]$.

Table 20. X-ray powder data of residue from pyrolysis.

$\theta/_2$	$[PCl_4^+][PF_6^-]$	$[PCl_4^+]F^-$
7·79	7·8	
9·20	9·0	
9·68		
10·68	10·6	10·8
11·38		
12·39		12·5
15·31	15·3	
15·78		15·6
16·35	16·5	16·7
18·60		
19·58		19·9
22·74	22·3	
23·75	23·4	23·7

The chlorine analysis from the solid product of pyrolysis gave a value of 60%. An attempted separation of $[PCl_4^+][PF_6^-]$ from $[PCl_4^+]F^-$ by sublimation, described by Kolditz, gave a chlorine analysis for the sublimate of 61·2%, with X-ray powder lines of both solids appearing. The preparation, as described by Kolditz, of liquid PCl_4F by distillation from a suspension of the sublimate in arsenic trichloride, was attempted. This procedure yielded a distillate which contained solid material, with a chlorine content, unchanged from above, of 61·2%. The chlorine content corresponding to the composition PCl_3F_2 is 60·8%. This composition could be attained by a mixture of 1 mole $[PCl_4^+][PF_6^-]$ and 2 mole $[PCl_4^+]F^-$ or by the formulation $[PCl_3F^+]F^-$, $[PF_4^+][PCl_6^-]$, or $[PCl_4^+][PCl_2F_4^-]$. However, the X-ray powder diagram shows it to be a mixture of $[PCl_4^+][PF_6^-]$ and $[PCl_4^+]F^-$, although the possibility of an intermediate, unstable with respect to these two compounds cannot be discounted. The fact that a composition very close to PCl_3F_2 has been obtained at so many stages in this preparation is strongly suggestive of a compound of this composition occurring at some point.

The preparation of $[PCl_4^+]F^-$ was repeated incorporating certain experimental modifications. It is likely that the PCl_4F first formed condensed and returned to the arsenic trichloride where the change to $[PCl_4^+]F^-$ occurs. A loss of PCl_4F by reaction with phosphorus pentafluoride to give $[PCl_4^+][PF_6^-]$ occurs in the condenser; by carrying out the pyrolysis reaction in a stream of dry nitrogen gas, it was hoped that the phosphorus pentafluoride might be removed more rapidly and thus formation of $[PCl_4^+][PF_6^-]$ prevented. The solid product obtained by this procedure was found to contain 61·0% chlorine; with both $[PCl_4^+][PF_6^-]$ and $[PCl_4^+]F^-$ present in the X-ray powder diagram. This material was itself pyrolysed thus ensuring the complete removal of phosphorus pentafluoride, pyrolysis being continued until no effluent gas was detectable. No solid material could be obtained from the solvent by crystallization in this instance. On repeating the pyrolysis with a further sample of $[PCl_4^+][PF_6^-]$ and examining quantitatively the gaseous products, it was found that 0·043 mole $[PCl_4^+][PF_6^-]$ gave 0·0041 mole PF_3Cl_2 and 0·0058 mole phosphorus pentafluoride (the yield of phosphorus pentafluoride calculated on the basis of conversion of $[PCl_4^+][PF_6^-]$ to PCl_4F is 0·0389 mole i.e. conversion was ca.1%). On this basis the expected yield of

$[PCl_4^+]F^-$ should be ca.1g. However, as was found in the previous experiment, no solid material could be isolated from the solvent. It was significant that the upper parts of the condenser were heavily coated with white solid material. It was concluded that the effect of the nitrogen stream was to blow the evolved molecular PCl_4F further up the condenser and allow greater opportunity for reaction with phosphorus pentafluoride to form $[PCl_4^+][PF_6^-]$ and not less as had been hoped.

Due to the lack of success achieved in the above experiments, it was thought that it might prove advantageous to consider an alternative medium for pyrolysis, for instance an organic solvent.

A preliminary investigation showed that carbon tetrachloride had suitable properties for this purpose. Accordingly a pyrolysis was carried out in this solvent together with a quantitative estimation of volatile products. The carbon tetrachloride was, however, found to appear in the condensate of the volatile pyrolysis products which made the separation of PF_3Cl_2 and phosphorus pentafluoride difficult, the I.R. spectra indicating that mixed solutions of phosphorus pentafluoride and PF_3Cl_2 in the solvent were obtained. The quantitative estimation of the effluent products was not possible and an accurate estimation of the expected solid yield could not be obtained. The solid product obtained from this preparation was found from its X-ray powder diagram to consist of $[PCl_4^+]F^-$ and $[PCl_4^+][PF_6^-]$. Certain unknown powder lines occurred and these lines were the same as those obtained from the first pyrolysis experiment in arsenic trichloride; the X-ray powder data is given in table 21.

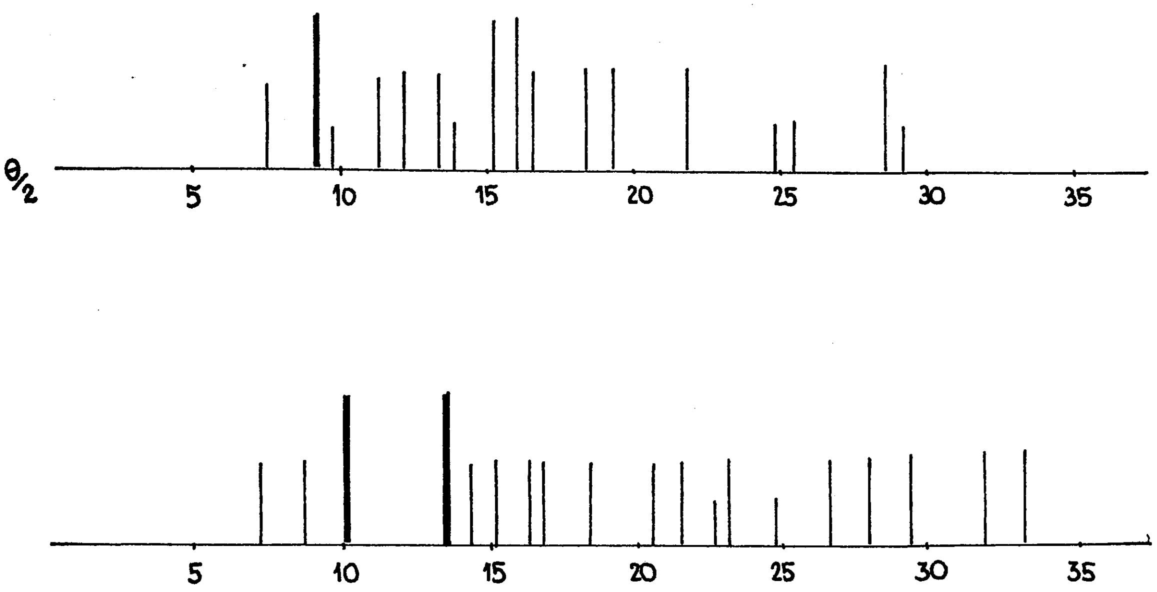
This experiment was repeated using a larger amount of starting material. The X-ray powder diagram of the solid product from this experiment is given in table 21 and figure 14. The solid was then sublimed at 80-85° in an atmosphere of dry air and the sublimate examined; the powder diagram showed no change indicating that the material had sublimed unchanged.

The X-ray powder pattern of this material is quite different from that of $[PCl_4^+][PF_6^-]$ and $[PCl_4^+]F^-$. This solid is different from any of those so far dealt with in the pyrolysis studies and it occurs alone, without $[PCl_4^+]F^-$ or $[PCl_4^+][PF_6^-]$. It is significant that these powder lines which remained unallocated in the previous

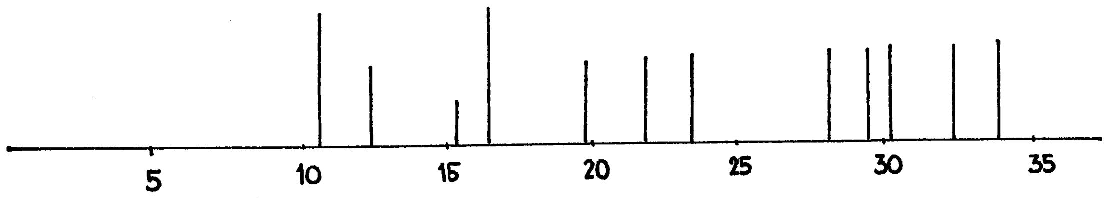
Table 21. X-ray data for solid from pyrolysis in carbon tetrachloride.

$\theta/_2$	$[PCl_4^+][PF_6^-]$	$[PCl_4^+]F^-$
7·80	7·80	
9·41 vs	9·0	
9·56	10·6 vs	10·8 vs
11·41	13·7 vs	
12·35		12·5
13·20		
13·94	14·6	
15·59 s	15·6	15·3
16·36 s		16·5 vs
16·87	17·2	
18·62	19·0	
19·95	21·2	19·9
22·04	22·3	21·9
23·42	23·0	23·4
24·90	23·7	
25·62	25·0	
28·90	27·1	28·3
29·40	28·3	29·5

Fig.14. The X-ray Powder Diagram of the Solid from Pyrolysis of $[PCl_4^+][PF_6^-]$ in Carbon Tetrachloride.



$[PCl_4^+][PF_6^-]$



$[PCl_4^+]F^-$

pyrolysis of $[PCl_4^+][PF_6^-]$ could be accounted for in the diagram of this new product.

In view of the evidence obtained from the X-ray data, a complete analysis of the solid material was carried out. The results for chlorine (gravimetrically), phosphorus (volumetrically) and fluorine (gravimetrically) are:

Chlorine	%	:	79·6	80·0	Mean:	79·8
Phosphorus	%	:	15·6	15·8		15·7
Fluorine	%	:	4·6	4·6		4·6
Total	%	:	99·8	100·4		100·1

Ratio P:Cl:F : 2·01:9·17:1

The analytical figures correspond to a compound of composition $PCl_{4\cdot5}F_{0\cdot5}$ i.e. P_2Cl_9F. It will be seen that this composition is intermediate between PCl_5 and PCl_4F. Since the material is solid it is reasonable to suggest that it is ionic in form. Two possibilities exist with such a case: either the fluorine is in the anion or the cation thus: $[PCl_4^+][PCl_5F^-]$ or $[PCl_3F^+][PCl_6^-]$. Kolditz has recently studied the corresponding bromine compoun P_2Cl_9Br postulated as $[PCl_4^+][PCl_5Br^-]$ (28); he offers no proof, however, that the bromine is anionic. An important observation, in this connection, is that the tetrahedral $[PCl_4^+]$ ion is more stable than the hexagonal $[PCl_6^-]$; an instance of this is the partial fluorination of phosphorus pentachloride solid to give $[PCl_4^+][PF_6^-]$ (15). It thus appears that the fluorine in P_2Cl_9F is anionic but further experiments were undertaken to confirm this.

QUANTITATIVE ELECTROLYSIS OF A SOLUTION OF P_2Cl_9F IN ACETONITRILE.

Two possibilities exist for the ionisation of P_2Cl_9F. Firstly, the fluorine may be in the anion giving rise to the ionisation scheme:

$$[PCl_4^+][PCl_5F^-] \rightleftharpoons [PCl_4^+] + [PCl_5F^-] \qquad (1)$$

or the fluorine may be cationic giving:

$$[PCl_3F^+][PCl_6^-] \rightleftharpoons [PCl_3F^+] + [PCl_6^-] \qquad (2)$$

The first ionisation scheme would lead to a decrease in the fluorine content of the cathode solution, the second scheme to an increase.

Suppose:

ΔF = increase in g.atoms of F at cathode.

t_+ = transport number of cation.

X = quantity of current passed (in Faradays).

Then for (1) $\Delta F = -Xt_+$

and for (2) $\Delta F = Xt_+$

The experimental result was as follows:

Increase in g.atoms F at anode = 0·000447

Decrease in g.atoms F at cathode = 0·000421

This result clearly indicates that the fluorine atom is located in the anion. The value of the transport numbers are:

		t_+	t_-
Derived from cathode	:	0·57	0·43
Derived from anode	:	0·59	0·41
Mean	:	0·58	0·42

The numerical values of the transport numbers strongly supports the idea that the ionic system must be described in the above form, for in systems in which the passage of current does not occur through a chain transfer process, the transport numbers of the ions are found to be approximately equal (i.e. ca.0·5). Since in this system a chain mechanism of conduction involving the solvent is improbable then the value of t_+ would be expected to be in the region of 0·5. The results of the experiment are thus satisfactory and the compound can be written $[PCl_4^+][PCl_5F^-]$.

The formation of $[PCl_4^+][PCl_5F^-]$, from $[PCl_4^+][PF_6^-]$, is accompanied by evolution of PF_3Cl_2 and phosphorus pentafluoride; no evidence of other compounds were found in the I.R. spectrum of the products. These observations thus support the reaction scheme as:

$$9[PCl_4^+][PF_6^-] \longrightarrow 4[PCl_4^+][PCl_5F^-] + 10PF_5.$$
$$[PCl_4^+][PF_6^-] \longrightarrow 2PF_3Cl_2$$

This electrolysis experiment was carried out in a specially designed cell, a description of which is included in the Appendix.

MOLAR CONDUCTANCE OF $[PCl_4^+][PCl_5F^-]$ IN ACETONITRILE SOLUTION

MOLAR CONDUCTANCE OF $[PCl_4^+][PCl_5F^-]$ IN ACETONITRILE SOLUTION

The conductance of $[PCl_4^+][PCl_5F^-]$ in acetonitrile solution was studied using a pipette type cell similar in design to that used in the study of PF_3Cl_2.

In marked contrast to PF_3Cl_2 the specific conductance of solutions of $[PCl_4^+][PCl_5F^-]$ did not vary with time.

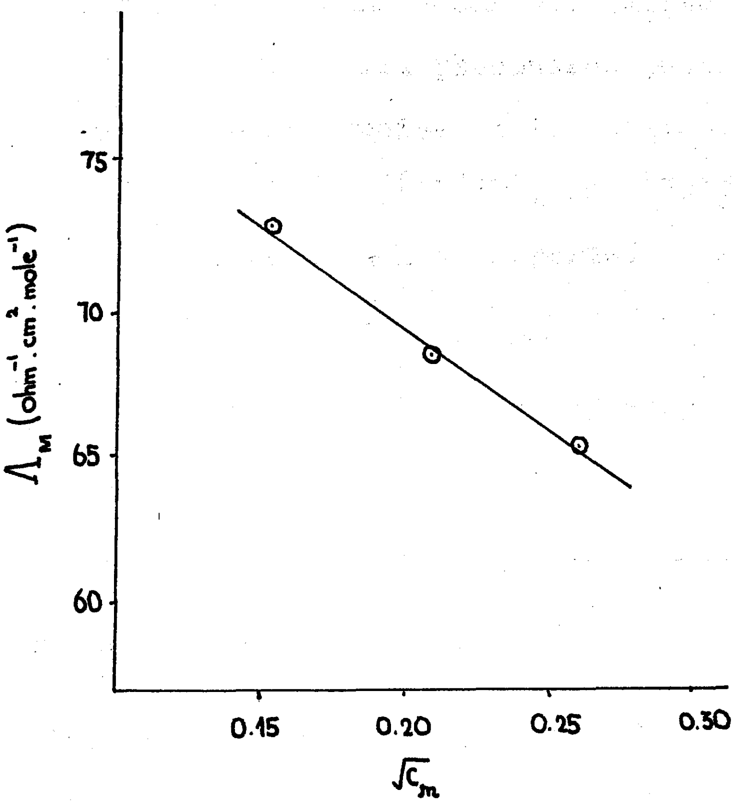
The results are set out in table 22 and figure 15.

Table 22. Conductance of $[PCl_4^+][PCl_5F^-]$ in Acetonitrile at 20°

c_m mole.litre^{-1}	$\kappa \times 10^4$ ohm.$^{-1}$cm.$^{-1}$	Λ m ohm.$^{-1}$cm.^{2} mole.$^{-1}$
0·0227	16·36	72·21
0·0433	29·65	68·53
0·0685	45·28	66·13

As can be seen from figure 15, these values of molar conductance when plotted against the square root of concentration fall on a straight line of negative slope.

Fig.15. The Conductance of $[PCl_4^+][PCl_5F^-]$ in Acetonitrile Solution.



The observation that the specific conductance does not vary with time in contrast to the results found in the case of PF_3Cl_2, is evidence that the time-variation effect is caused by an ion-formation process. If this is so, then it might be expected that no variation of conductance with time would occur with acetonitrile solutions of the ionic solid phosphorus pentahalides. Thus, in the course of studies of the solid ionic pentahalides $[PCl_4^+][PF_6^-]$, $[PCl_4^+]F^-$, and $[PCl_4^+][PCl_5Br^-]$ Kolditz and his co-workers have reported no such time-variation effect occuring.

In general, phosphorus pentahalides are thought to ionise in acetonitrile solution thus:

$$2PX_5 \longrightarrow [PX_4^+][PX_6^-] \rightleftharpoons [PX_4^+] + [PX_6^-].$$

where X is a halogen atom.

All the available data on compounds of this general type is set out in table 23 and figure 16. It is interesting to note the large variation in conductance found by Kolditz in his studies of the ionic pentahalides. Of the pentahalides so far reported, the ionic solid $[PCl_4^+][PF_6^-]$ appears to have a very high conductance in

Table 23. The Conductance of Compounds of Phosphorus V in Acetonitrile at 0·0485M.

(Values extrapolated or interpolated to this concentration from graphical presentation).

	Compound.	Λ_m ohm.$^{-1}$cm.^{2} mole.$^{-1}$	Temp °C	Reference.
1.	$P(CF_3)_2Cl_3$	0·7	15°	(30)
2.	$[PCl_4^+][PCl_5Br^-]$	1·1	17°	(29)
3.	$[PCl_4^+]F^-$	7·0	21°	(16)
4.	PF_3Cl_2	9·6	20°	
5.	PBr_5	10·0	25°	(22)
6.	PF_5	10·6	20°	(31)
7.	PCl_5	30·2	25°	(24)
8.	$P(CF_3)_3Cl_2$	41·8	15°	(30)
9.	$[PCl_4^+][PCl_5F^-]$	68·0	20°	
10.	$P(OPh)_3Cl_2$	85·6	25°	(32)
11.	$[PCl_4^+][PF_6^-]$	98·0	30°	(15)

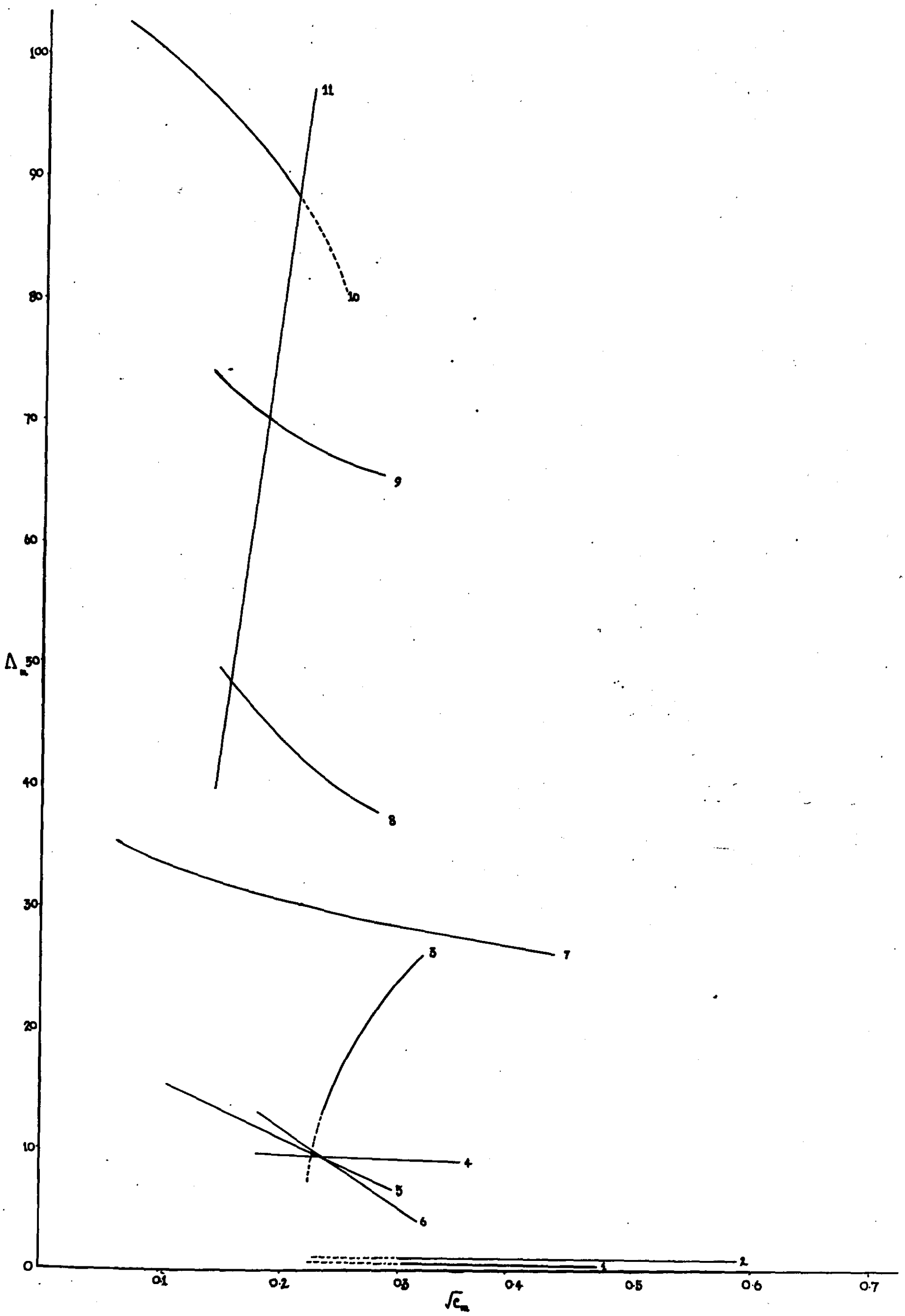


Fig.16. Comparison of the Molar Conductance of Phosphorus Pentahalides in Acetonitrile Solution.

acetonitrile solutions. The solid $[PCl_4^+][PCl_5F^-]$ discovered in this present work, has a conductance intermediate between that of $[PCl_4^+][PF_6^-]$ and phosphorus pentachloride $[PCl_4^+][PCl_6^-]$. It would seem from this observation, that the conductance value is connected with the electronegativity of the ligand atoms in the anion. This tentative rule raises an interesting point: no evidence is to hand which proves that the structure of "$[PCl_4^+]F^-$" is not in fact $[PCl_4^+][PCl_4F_2^-]$, a more commonly met with form in phosphorus pentahalides. The conductance value expected of such a compound would be intermediate between $[PCl_4^+][PF_6^-]$ and $[PCl_4^+][PCl_5F^-]$. However, the experimental value is lower than that for both these compounds and suggests that the structure is $[PCl_4^+]F^-$ rather than $[PCl_4^+][PCl_4F_2^-]$. The theory would predict the conductance value of phosphorus pentabromide to be considerably lower than that of phosphorus pentachloride, and experimental work shows this to be the case. With regard to phosphorus pentafluoride, however, the rule apparently no longer holds, since the highest conductance of all might be expected for this compound. If phosphorus pentafluoride behaves like phosphorus pentahalides in general, then in acetonitrile, an ionisation scheme of the following form would be expected.

$$2PF_5 \rightleftharpoons [PF_4^+] + [PF_6^-].$$

However, the $[PF_4^+]$ ion might be expected to be an unlikely species thus favouring the establishment of the equilibrium on the molecular side and thereby producing a low conductance value.

The position with regard to phosphorus pentabromide is complicated in the following way: It has been observed that in acetonitrile solution, phosphorus pentabromide undergoes some degree of molecular dissociation which may involve the molecular pentahalide (22), in addition to the ionic dissociation process, thus:

$$[PBr_4^+]Br^- \longrightarrow PBr_5 \rightleftharpoons PBr_3 + Br_2$$

- this behaviour may contribute to the value of the conductance being much lower than might be expected for an ionic compound.

The surprisingly large difference in the conductance of $P(CF_3)_2Cl_3$ and $P(CF_3)_3Cl_2$ has been commented on by Emeléus and Harris (29). The former compound is thought to have the trigonal bipyramidal molecular configuration with the three chlorine atoms occupying the planar positions, thus forming a highly symmetrical system. The latter compound, however, is thought to be a mixture of isomers in which the chlorine atoms occupy both planer and apical positions. The large difference existing between the conductance of these two compounds, is thought to be a manifestation of the relative symmetry of the molecules. It may be that the high conductance value exhibited by $P(OPh)_3Cl_2$ solutions is connected with the occurrence of isomers and, moreover, suggests that an ionic dissociation is more favoured than a molecular dissociation leading to formation of triphenyl phosphite and chlorine.

It is probable that ion size plays an important part in the determination of the magnitude of conductance exhibited by a particular compound. However, after considering the information set out in table 22 it is not clear what relationship exists. Whilst from the above discussion it does not appear possible to formulate any empirical rule involving ion size and electronegativity, which enables the conductance of phosphorus pentahalides in acetonitrile to be predicted. Conductance of such pentahalide solutions in acetonitrile is due first to ionisation of the compounds, followed by ion solvation by the acetonitrile. Thus, it may be the relative ease or difficulty with which the solvent molecules cause solvation of the different ions which, in the main, controls the magnitude of the conductance.

THE MASS SPECTRUM OF $[PCl_4^+][PCl_5F^-]$ VAPOUR.

It has been shown that the vapour phase in equilibrium with the solid $[PCl_4^+][PF_6^-]$ is PF_3Cl_2. It was thus of interest to study the vapour phase in equilibrium with $[PCl_4^+][PCl_5F^-]$: this was attempted by a mass spectrometric investigation.

Since the study of PF_3Cl_2, the mass range of the mass spectometer had been extended to ca.450; the mass definition was however, subject to error especially in the high mass region $>$ 200 and a limit of ±8 mass units was applied.

The details of the spectrum at an ionisation voltage of 50e.v. are given in table 24. Because of the reduced definition mentioned above, only the highest and lowest mass value for each peak is given. It is seen that peaks can be assigned to the ion species $P_2Cl_8F^+$, $P_2Cl_7F^+$, $P_2Cl_6F^+$, $P_2Cl_5F^+$, $P_2Cl_3F^+$, $P_2Cl_2F^+$ and P_2ClF^+ in addition to various fragments containing one phosphorus atom.

These results are very significant as they clearly indicate the presence in the vapour phase of species containing two phosphorus atoms. For comparison the spectrum of phosphorus pentachloride vapour was observed;

the results are given in table 25. The cracking pattern showed peaks which have been assigned to the ion species $P_2Cl_9^+$, $P_2Cl_7^+$, $P_2Cl_5^+$, $P_2Cl_4^+$, $P_2Cl_3^+$, $P_2Cl_2^+$ and P_2Cl^+ as well as a collection of peaks corresponding to species containing one phosphorus atom.

Recent investigation has indicated the existence of polymerised metallic halides in the vapour state (33). However, whilst it has been known for many years that the halides of phosphorus V are based largely on ionic lattices, the considerable amount of information on the vapour densities, particularly of phosphorus pentachloride (see later) has provided evidence only of dissociation, never of association. It is clear, however, from the mass spectra that association does occur.

The existence of P_2X_{10} fragments where X represents Cl or F) and associated fragments in the mass spectrometer could be explained by a collision hypothesis e.g.

$$PX_5 \quad + \quad PX_5^+ \quad \longrightarrow \quad P_2X_{10}^+$$

but in view of the absence of fragments containing two fluorine atoms in the experiment with P_2Cl_9F and the relatively small amounts of PX_5 species likely to be present

Table 24. Mass Spectrum of $[PCl_4^+][PCl_5F^-]$ Vapour at 50e.v.

Mass.No.	Assignment.	Required.
31	P^+	31
35,37	Cl^+	35,37
66,69	PCl^+	66,68
85,87	$PClF^+$	85,87
102-106	PCl_2^+	101-105
117,119	P_2ClF^+	116,118
113,135	$P_2Cl_2^+$	132-136
136-140	PCl_3^+	136-142
152-156	$P_2Cl_2F^+$	151-155
166-173	PCl_4^+	171-179
183-186	$P_2Cl_3F^+$	186-192
258-266	$P_2Cl_5F^+$	256-266
280-290	$P_2Cl_6F^+$	291-303
305-318	$P_2Cl_7F^+$	326-340
358-376	$P_2Cl_8F^+$	361-377

Table 25. The Mass Spectrum of $[PCl_4^+][PCl_6^-]$ Vapour at 50e.v.

Mass No.	Assignment.	Required.
380-370	$P_2Cl_9^+$	377-395
303-313	$P_2Cl_7^+$	307-321
234-240	$P_2Cl_5^+$	237-247
196-203	$P_2Cl_4^+$	202-210
165-170	$P_2Cl_3^+$	167-173
129-132	$P_2Cl_2^+$	132-136
97,99	P_2Cl^+	97,99
206-212	PCl_5^+	206-212
170-177	PCl_4^+	171-179
136-142	PCl_3^+	136-142
102-106	PCl_2^+	101-105
66,68	PCl^+	66,68
154-156	$POCl_3^+$	152-158
115-117	$POCl_2^+$	117-121
85,87	$POCl^+$	82,84
35,37	Cl^+	35,37

this seems unlikely. It is also possible that a parent of even higher molecular weight occurs, and that this on ionisation breaks up to give P_2X_{10} etc. units. However, the most reasonable hypothesis is that there are P_2X_{10} units in equilibrium with the solid at room temperature. The solid being of the type $[PX_4^+][PX_6^-]$, the units are formed essentially by evaporation of a cation-anion pair from the surface of the crystal.

In the P_2X_{10} and other P_2 units a halogen bridge involving a four membered ring could be possible. This would be in keeping with many other polymeric halides, and indeed, might be likely in that the resulting complex would have octahedrally disposed halogens around the phosphorus atoms, rather than the trigonal bipyramid arrangement, as found in the case of the phosphorus pentachloride molecule (18). The exact composition of the vapour with respect to monomeric and dimeric units in equilibrium with the solid and the detailed structure of these units remains to be investigated.

VAPOUR PHASE STUDY OF $[PCl_4^+][PCl_5F^-]$.

The results of the mass spectrum of $[PCl_4^+][PCl_5F^-]$ vapour show that the species P_2Cl_9F exists in the vapour phase which is in equilibrium with the solid at room temperature. However, no indication of the extent to which the dimerisation process occurs can be deduced from the experimental results. The mass spectrum of phosphorus pentachloride shows the presence of P_2Cl_{10} units in the vapour phase but molecular weight measurement shows the vapour to consist of PCl_5 and its dissociation products. Furthermore, in the case of $[PCl_4^+][PF_6^-]$ molecular weight measurements at 140° indicate the vapour phase to be largely monomeric PF_3Cl_2. From these considerations, it would seem unlikely that the vapour phase in equilibrium with $[PCl_4^+][PCl_5F^-]$ is principally P_2Cl_9F.

The pressure of a known volume and mass of $[PCl_4^+][PCl_5F^-]$ vapour was measured over the temperature range 110-210° in an apparatus similar to that used in the pyrolysis of PF_3Cl_2 and of $[PCl_4^+][PF_6^-]$. The results are recorded in table 25 and figure 17. From the graph, it is seen that above 110° the plot of pressure versus temperature is linear corresponding to complete vapourisation of the solid.

Table 26. The Pyrolysis of $[PCl_4^+][PCl_5F^-]$.

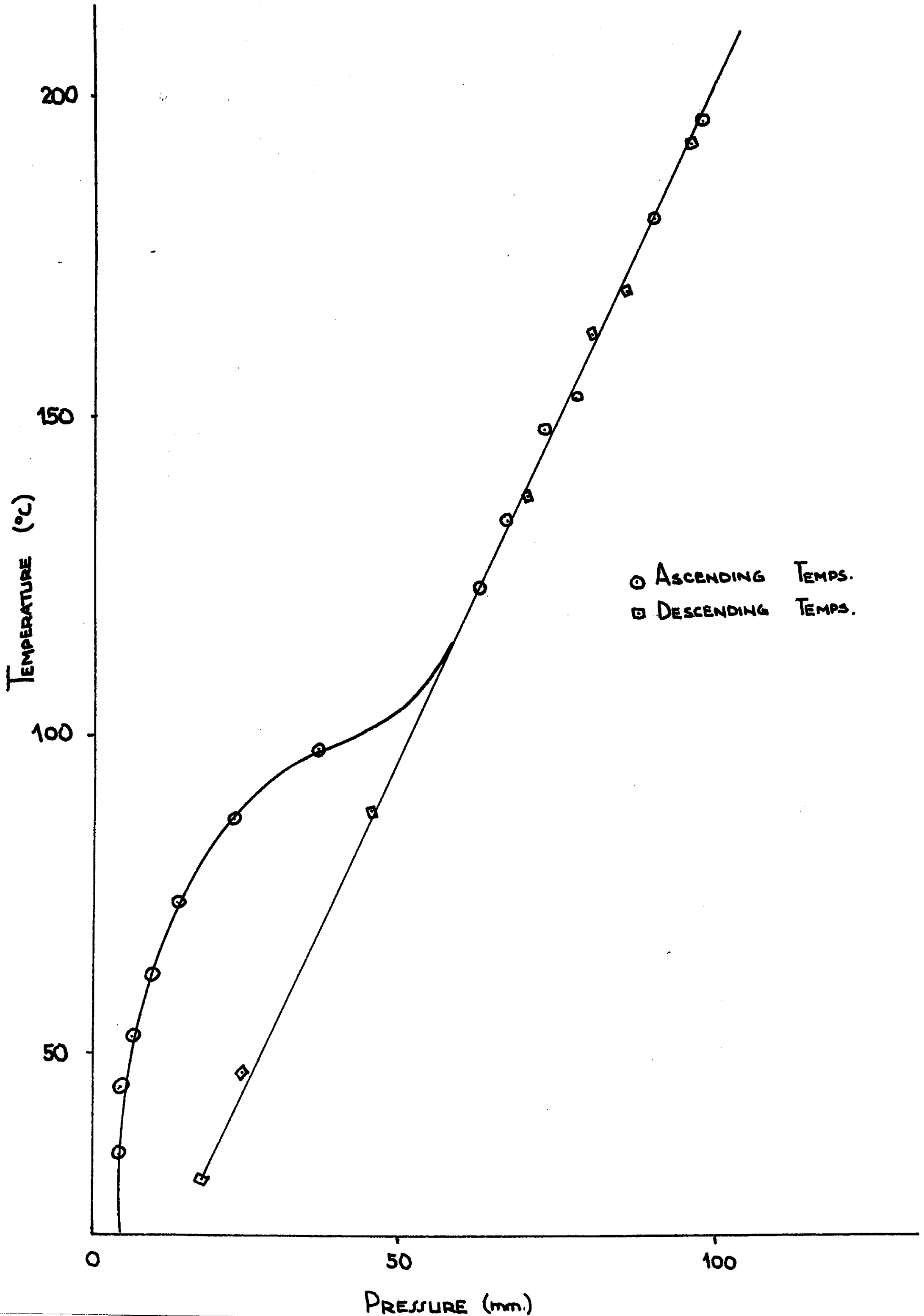
Pressure mm.	Temp. °C	Pressure mm.	Temp. °C
6·56	21·5	71·31	148·0
7·00	34·0	79·30	163·5
9·11	51·8	89·92	182·3
10·18	61·5	95·68	193·5
14·58	72·3	104·36	212·5
8·53	44·5	98·20	197·1
23·44	85·5	86·27	171·5
37·00	98·0	78·45	153·5
19·18	69·1	70·97	136·3
54·36	109·0	62·80	112·0
60·17	122·8	44·71	88·3
65·27	133·8	21·71	45·5
		17·00	23·5

Thus it is possible to calculate the apparent molecular weight of the vapour at any temperature between 110° and 220°. This was done for several temperatures and the results obtained are shown in table 27.

Table 27. Molecular Weight of $[PCl_4^+][PCl_5F^-]$ Vapour.

Temp. °C	M.W. (Theor:400·5).
109·0	198·4
122·8	185·7
133·8	176·0
148·0	166·6
163·5	155·3
182·3	143·0
193·5	137·6
212·5	131·2
197·1	135·2
171·5	145·4
153·5	153·4
136·3	162·9
112·0	173·1

Fig.17. The Pyrolysis of $[PCl_4^+][PCl_5F^-]$.



The value of the molecular weight at 109° i.e. just after complete vapourisation of the solid has taken place, is half the theoretical value for $[PCl_4^+][PCl_5F^-]$. Thus the amount of P_2Cl_9F if any, present in the vapour phase is small.

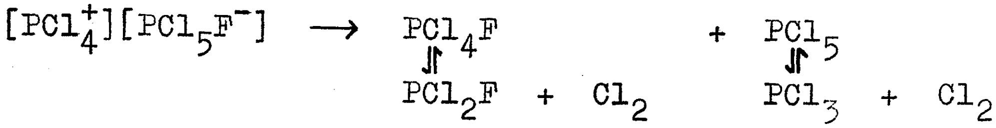
The observed molecular weight value at 109° can be interpreted at and above this temperature as indicating that the vapour phase is comprised of phosphorus pentachloride and PCl_4F i.e.

$$[PCl_4^+][PCl_5F^-] \longrightarrow PCl_4F + PCl_5$$

The species PCl_5 is known to undergo thermal dissociation and previous experiments have shown that PCl_4F behaves similarly. As already discussed in the pyrolysis of PF_3Cl_2, dissociation of PCl_4F to yield chlorine is favoured.

From these results and the data for the dissociation of phosphorus pentachloride, the dissociation of PCl_4F can be investigated further, thus:

In the system:



$$\begin{array}{lllllll} [PCl_4^+][PCl_5F^-] & \longrightarrow & PCl_4F & & + & PCl_5 & \\ & & \rightleftharpoons & & & \rightleftharpoons & \\ & & PCl_2F & + \; Cl_2 & & PCl_3 & + \; Cl_2 \end{array}$$

if the dissociation of the $[PCl_4^+][PCl_5F^-]$ is complete then let n mole of PCl_5 and PCl_4F be produced and the degree of dissociation of PCl_5 be x and of PCl_4F be y, then at equilibrium the total number of moles present will be

$$n(1-x) + n(1-y) + 2nx + 2ny$$

$$= n(2+x+y).$$

and the partial pressures of PCl_5, PCl_4F, PCl_3, and Cl_2 for a total pressure of P will be:

$$p_{PCl_5} = \frac{(1-x)}{(2+x+y)}P$$

$$p_{PCl_4F} = \frac{(1-y)}{(2+x+y)}P$$

$$p_{PCl_3} = \frac{(1-y)}{(2+x+y)}P$$

$$p_{Cl_2} = \frac{(x+y)}{(2+x+y)}P$$

The dissociation constants of PCl_5 and PCl_4F will thus be given as:

$$Kp_{PCl_5} = \frac{(x^2+xy)P}{(1-x)(2+x+y)}$$

$$Kp_{PCl_4F} = \frac{(y^2+xy)P}{(1-y)(2+x+y)}$$

Kp_{PCl_5} can be calculated from the equation of Fischer and Jubermann (27) and thus values of x can be found. The value of (2+x+y) can be obtained from the experimental results.

$$\text{M.W.(found)} = \frac{\text{M.W.(theor.)}}{\text{total no.moles.}}$$

$$= \frac{400 \cdot 5}{2+x+y}$$

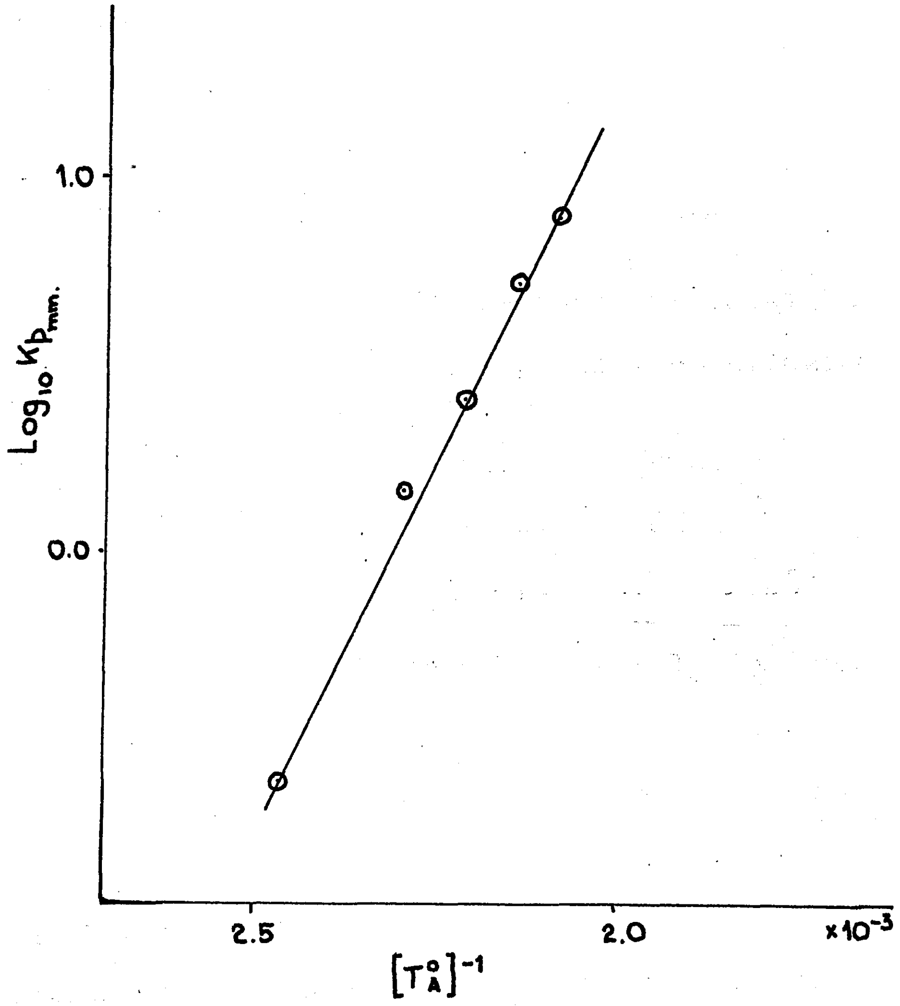
This procedure enables values of y to be calculated and thus Kp_{PCl_4F} can be found. The results of this calculation are shown in table 28; a plot of logKp versus T^{-1} is given in figure 18.

A comparison of the values of Kp from this experiment and these obtained from the pyrolysis of PF_3Cl_2 is shown in figure 19. The results derived from the pyrolysis of PF_3Cl_2 are lower than those obtained from the study of $[PCl_4^+][PCl_5F^-]$. It must be noted, however, that the pyrolysis of PF_3Cl_2 resulted in the formation of silicon

Table 28. Dissociation Constant of $PCl_4F \rightleftharpoons PCl_2F + Cl_2$.

$\log Kp_{PCl_5}$	(2+x+y)	Pressure mm.
-0·283	2·0187	54·36
0·146	2·1567	60·17
0·385	2·2756	65·27
0·862	2·4048	71·31
1·250	2·5770	79·30
1·706	2·8040	89·92
1·951	2·9106	95·68
2·344	3·0540	104·36
x	**y**	**$\log Kp_{PCl_4F}$**
0·5063	-0·4877	——
0·2425	-0·0858	——
0·2456	0·0300	-0·6120
0·3775	0·0275	-0·6630
0·5003	0·0769	0·1701
0·7127	0·0913	0·4060
0·7494	0·1612	0·7593
0·8596	0·1944	0·9393

Fig.18. Calculated Equilibrium Constants for the Dissociation: $PCl_4F \rightleftharpoons PCl_2F + Cl_2$.



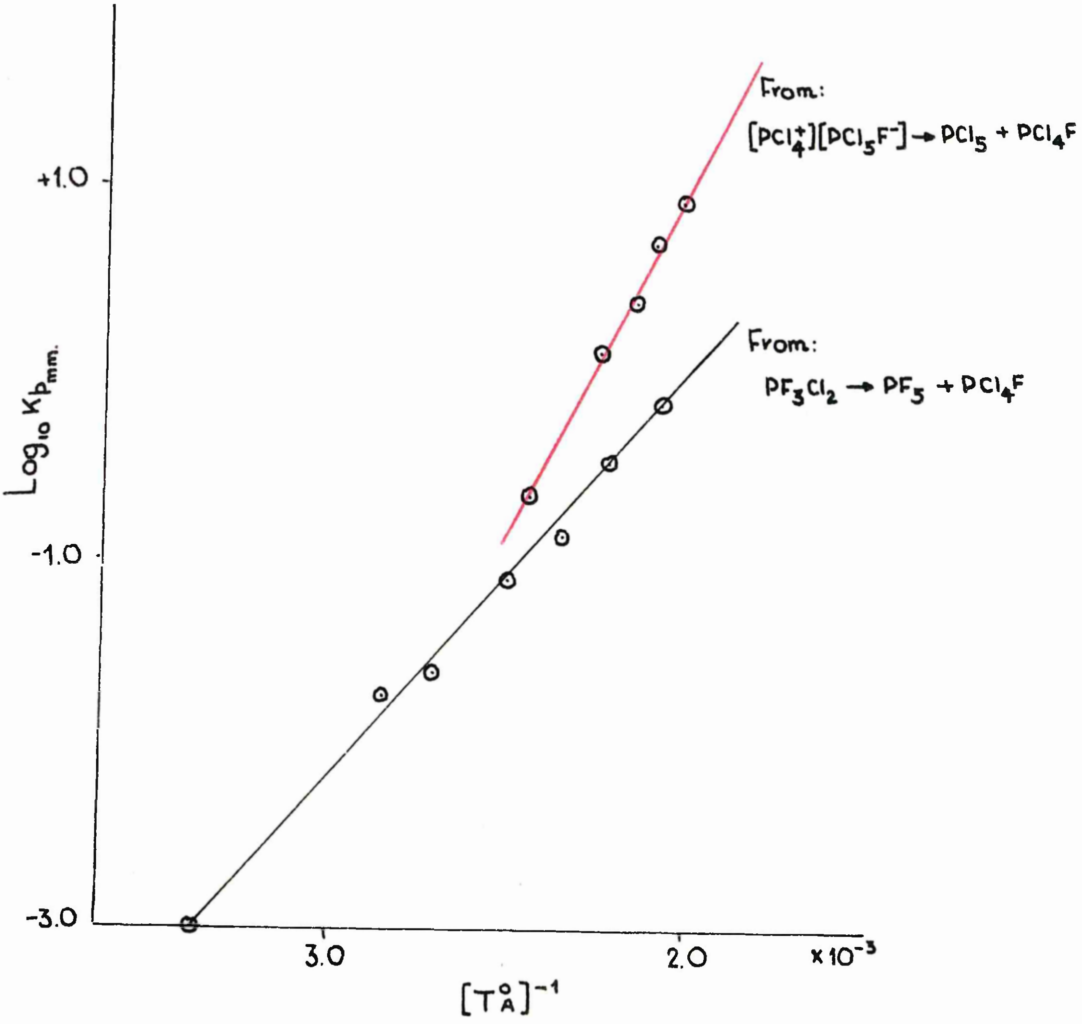
tetrafluoride and phosphorus oxyfluoride, which were not taken into account when the equilibrium constants of dissociation were derived. These gases would act as diluents in the equilibrium envolving PCl_4F and would produce overall, a somewhat lower value for the equilibrium constant. No significant amounts of diluent gases were found in the pyrolysis of $[PCl_4^+][PCl_5F^-]$, thus the dissociation constants derived from this study are the more reliable values.

The I.R. spectrum of the residual volatile phase after pyrolysis was completed, had the following details:

794s, 830m, 888m,
906w, 999s, 1405m,
1425m, 1430m. $cm.^{-1}$

The triplet at ca.1420 is very strongly indicative of phosphorus oxyfluoride, the remaining frequencies do not correspond with any known phosphorus halide spectrum. It is important, however, to note that these unallocated frequencies are identical with those occurring in the spectra of the products of pyrolysis of PF_3Cl_2 and tentatively related to PCl_4F. This observation supplies

Fig.19. Comparison of the Dissociation Constants for the Reaction: $PCl_4F \rightleftharpoons PCl_2F + Cl_2$.



weight to the theory that the disproportionation of $[PCl_4^+][PCl_5F^-]$ results in the formation of PCl_4F and phosphorus pentachloride, and, in doing so, supports the claim that pyrolysis of PF_3Cl_2 also involves formation of PCl_4F.

The following frequencies can now be tentatively assigned to PCl_4F:

798s, 830m, 888s,
906m. $cm.^{-1}$

PART III

VAPOUR PHASE STUDY OF PHOSPHORUS PENTACHLORIDE.

VAPOUR PHASE STUDY OF PHOSPHORUS PENTACHLORIDE.

Measurement of the vapour pressure of phosphorus pentachloride has been undertaken by several workers of which Fischer and Jübermann have carried out the most detailed investigation. The temperature range over which the measurements were made is, however, somewhat limited and in view of the importance of phosphorus pentachloride in the study of PF_3Cl_2, it was decided to attempt to extend the temperature range. This also presented a good opportunity of surveying the published data on the vapour phase of phosphorus pentachloride; the results of this survey are presented herewith.

The pressure of phosphorus pentachloride vapour was measured over a range of temperatures by a static (spoon gauge) method, and the results are recorded in table 29. For comparison purposes the results of Smith and Calvert (34) and of Fischer and Jübermann (27) are also given in tables 30 and 31 and are compared graphically in figure 20.

The experimental method employed by Smith and Calvert is rather unsatisfactory: a dynamic method of pressure

Table 29. Vapour Pressure of Phosphorus Pentachloride.

Temp. °C	Press. mm.	Experim.	Temp. °C	Press. mm.	Experim.
113•9	67•15	3	100•8	39•98	2
130•2	157•36	3	98•7	34•77	2
132•4	155•63	3	96•9	31•81	2
123•8	107•57	3	95•0	28•29	2
104•9	51•79	3	90•9	22•32	2
108•5	61•05	3	86•5	17•35	2
47•1	2•02	2	71•8	7•39	2
62•5	4•73	2	43•5	1•91	1
77•7	12•14	2	59•3	4•07	1
87•5	20•95	2	71•5	7•96	1
92•7	25•95	2	91•5	24•64	1
96•0	31•28	2	94•5	29•26	1

Vapour pressure equation:

$$\log_{10}p_{mm} = -2886{\cdot}2T^{-1} + 9{\cdot}314.$$

Table 30. Vapour Pressure of Phosphorus Pentachloride.

(Fischer and Jübermann).

Vapour pressure equation:

$$\log_{10}p_{mm} = \frac{-16,100T^{-1}}{4\cdot57} + 11\cdot034$$

Temp. °C	Press. mm.	Temp. °C	Press. mm.
100·5	40·2	140·6	340·0
108·2	60·5	147·4	446·3
111·6	75·1	147·6	456·7
117·6	110·7	148·2	451·3
120·8	115·8	149·0	489·7
127·7	178·1	151·1	540·0
132·5	222·0	151·6	543·7
133·3	228·8	152·3	587·1
133·9	238·0	153·6	581·9
136·5	276·1	157·8	712·4
140·3	335·4	158·1	721·8

Table 31. Vapour Pressure of Phosphorus Pentachloride.

(Smith and Calvert).

Press mm.	Temp. °C	Press. mm.	Temp. °C
31	98·08	492	152·48
60	108·31	608	157·63
158	126·10	748	162·58
219	132·70	915	166·89
347	143·68		

measurement was employed and reaction between the phosphorus pentachloride and the paraffin oil employed may lead to inaccuracy.

The method used by Fischer and Jübermann is also somewhat unsatisfactory in that they noted a rather high residual pressure after the experiments had been completed; this residual pressure amounted to as much as 25 mm.

The results of the present study lead to a value of the sublimation temperature of 175·5°. This value can be compared with:

148°	Landolt and Börnstein.	(35)
149°	Biltz and Jeep .	(36)
163-164	Sugden.	(37)
159-1604	Moureu, Magat and Wetroff.	(38)
159°	Fischer and Jübermann.	(27)

From figure 20 it is seen that the vapour pressure curve obtained from this work shows a noticeable deviation from the curve obtained by Fischer and Jübermann. In this connection, a significant observation has been made by Popov and his co-workers in the course of an investigation of the addition of bromine to phosphorus trichloride (23). It was reported by these workers that if phosphorus pentachloride is rapidly sublimed under reduced pressure, a hitherto unknown crystalline modification is obtained, quite different from the tetragonal form. The method of purification used in this present study was by sublimation in vacuo. The X-ray powder diagram of a sample sublimed as in the case of the sample used for the vapour pressure measurement was measured and compared with existing data. The comparison is set out diagrammatically in figure 21. (The method of purification adopted by Kolditz is not quoted in his paper). A method was evolved enabling values of the d-spacing to be obtained from the single crystal study of Clark, Powell and Wells (39); details of this method are included in the Appendix. The most striking feature of figure 21, is that no two patterns can be exactly matched. There is a close similarity between patterns D and E, Popov's "normal" form and the sublimed form used in this present investigation. Popov's sublimed form, pattern C differs rather markedly from the sublimed form in pattern E. It is, thus, not possible to draw any definite conclusions from a consideration of these X-ray powder patterns. Certainly, it appears that the crystalline form taken up by phosphorus pentachloride depends critically on the method of purification adopted. No X-ray data on the samples of phosphorus pentachloride used by Fischer and Jübermann is quoted. The method of purification used, namely, sublimation in a stream of chlorine is different from that of this present work and possibly produces a unique crystalline form. This possibility, together with the rather unsatisfactory method of measuring the vapour pressure, employed by Fischer and

Fig.20. The Vapour Pressure of Phosphorus Pentachloride.

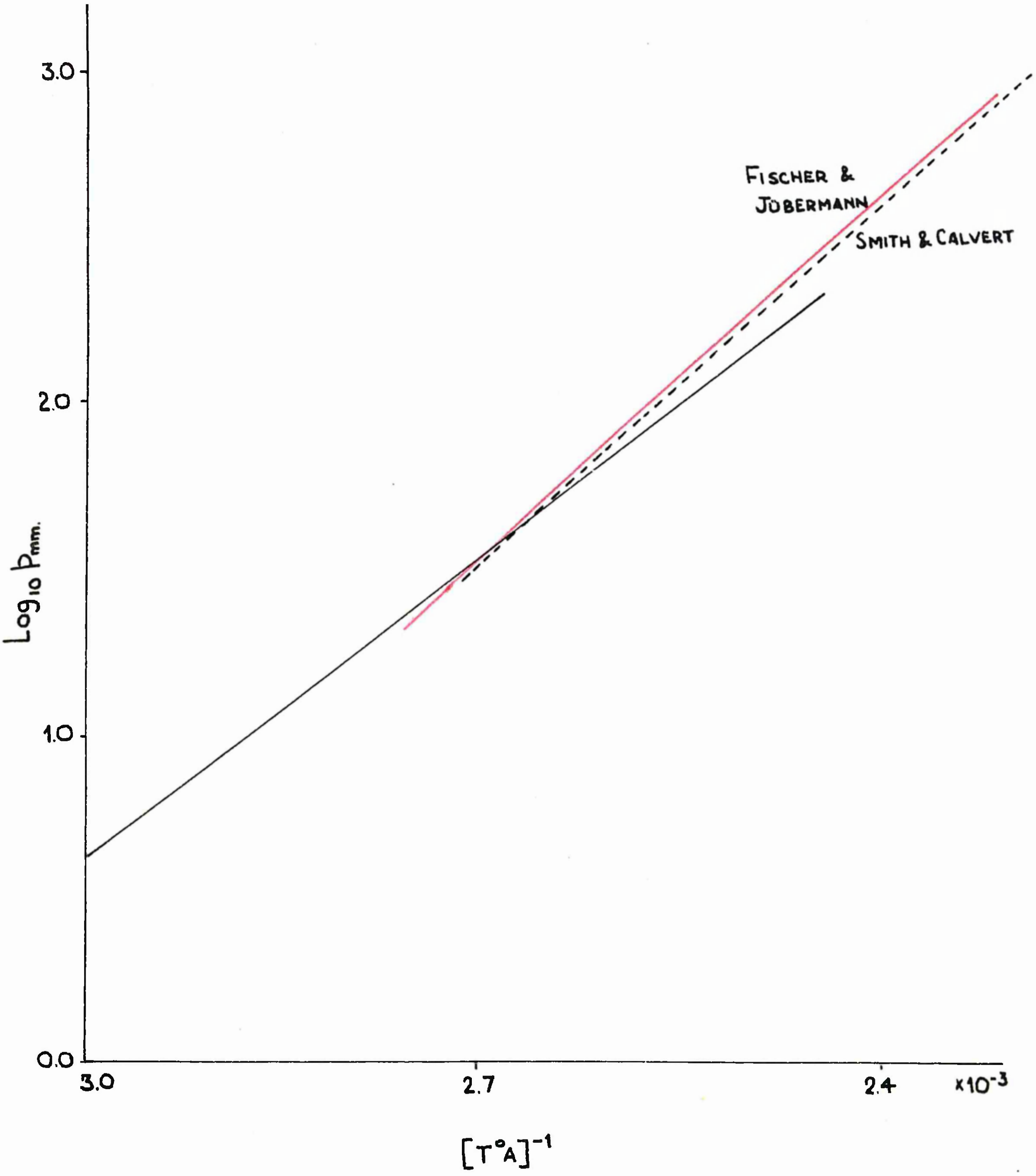
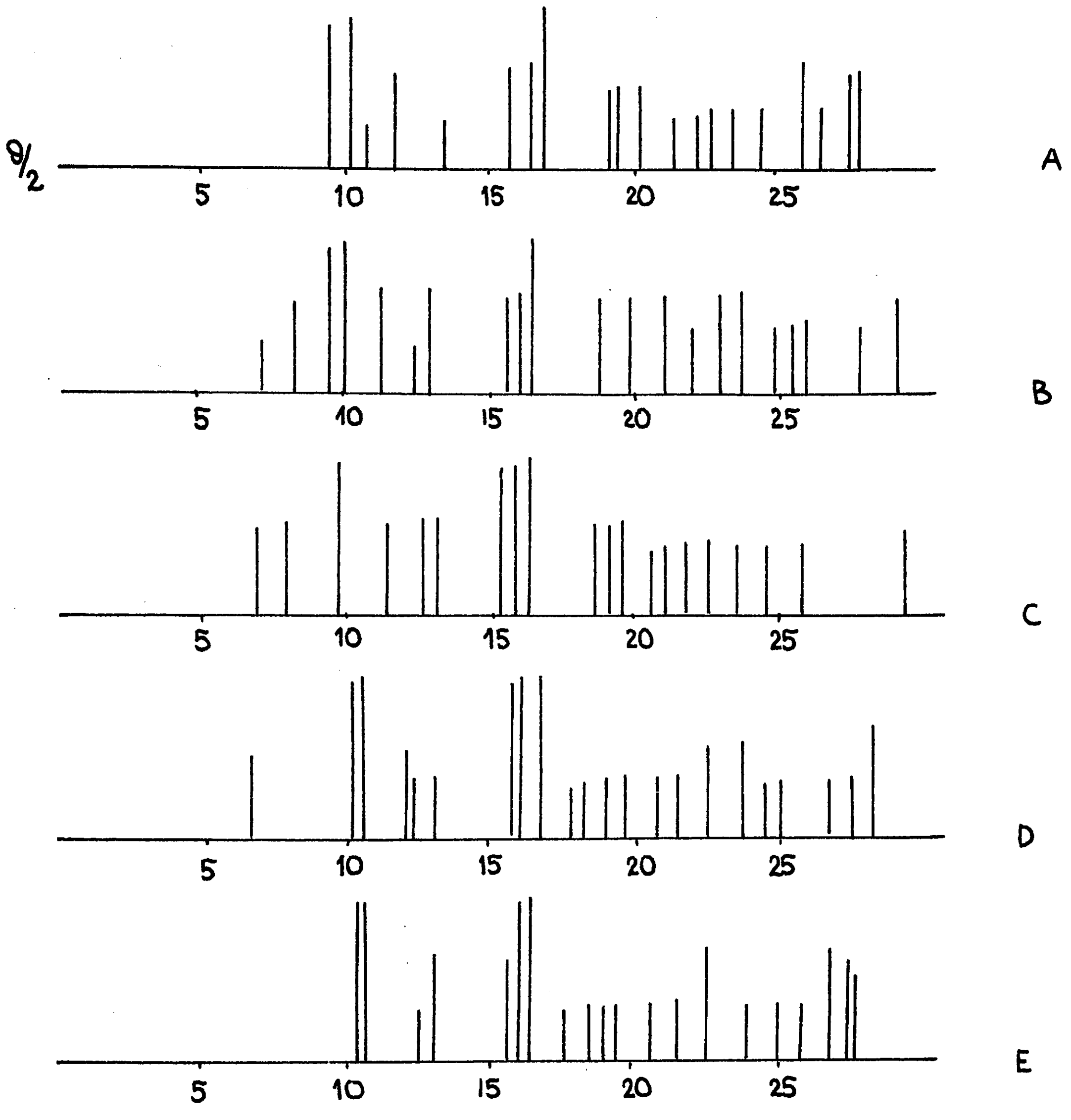


Fig.21. X-ray Powder Diagrams of Phosphorus Pentachloride.



A : Kolditz (15)
B : Clarke et al (39) : recrystallised
C : Popov (12) : sublimed
D : Popov (12) : 'normal'
E : Present work : sublimed.

Jubermann, may provide an explanation of the variation between the results of their work and this present study. No definite conclusions can be drawn, however, without further experimental investigation.

Between 140° and 170°, the apparent molecular weight of a known volume and mass of phosphorus pentachloride vapour, was calculated. This was done for several temperatures and the results, expressed in terms of $\log_{10}Kp_{mm}$ are set out in table 32. A survey of all the available results of investigation of the vapour phase dissociation of phosphorus pentachloride, is given in tables 33a,b,c. The results are compared in figure 22. The vapour density equation calculated accurately by the method of least squares, is:

$$\log_{10}Kp_{mm} = -4{\cdot}653T^{-1} + 11{\cdot}883$$

From the equation, the heat of dissociation for

$$PCl_{5(g)} \longrightarrow PCl_{3(g)} + Cl_{2(g)}$$

is 21·4 K.cal./mole (c.f. F and J's value 22·0 K.Cal./mole).

The most striking feature of this study of phosphorus pentachloride, is the evidence obtained from the X-ray powder studies. This suggests that no single substance

Table 32. The dissociation of phosphorus pentachloride in the vapour phase.

Temp °C	Press mm.	a	$Kp_{mm.}$	$\log_{10}Kp_{mm.}$
140·9	201·2	0·036	0·261	-0·583
142·0	214·4	0·101	2·209	0·344
145·1	226·3	0·153	5·425	0·734
150·9	237·9	0·196	9·499	0·978
155·2	241·1	0·199	9·716	0·986
158·0	249·6	0·285	15·46	1·160
166·6	260·4	0·263	19·93	1·287
170·5	269·9	0·294	25·48	1·406

Survey of results of the investigation of the vapour phase dissociation of phosphorus pentachloride.

Table 33a.

Temp °C	$\log Kp_{mm.}$	Temp. °C	$\log Kp_{mm.}$
105·4	-0·330	128·8	0·524
106·2	-0·177	133·2	0·505
108·0	-0·069	137·5	0·633
111·1	0·136	143·9	0·708
112·2	0·129	144·2	0·769
119·0	0·222	148·3	0·861
122·2	0·288	154·8	0·985
125·5	0·341	158·0	1·023

(40)

Table 33b.

Temp °C	$\log_{10}Kp_{mm.}$	Temp °C	$\log_{10}Kp_{mm.}$
166	1·311	301	3·852
170	1·398	340	4·487
189	1·682	350	4·506
212	2·270	358	4·610
261	3·180	222	2·297
283	3·576	258	4·618

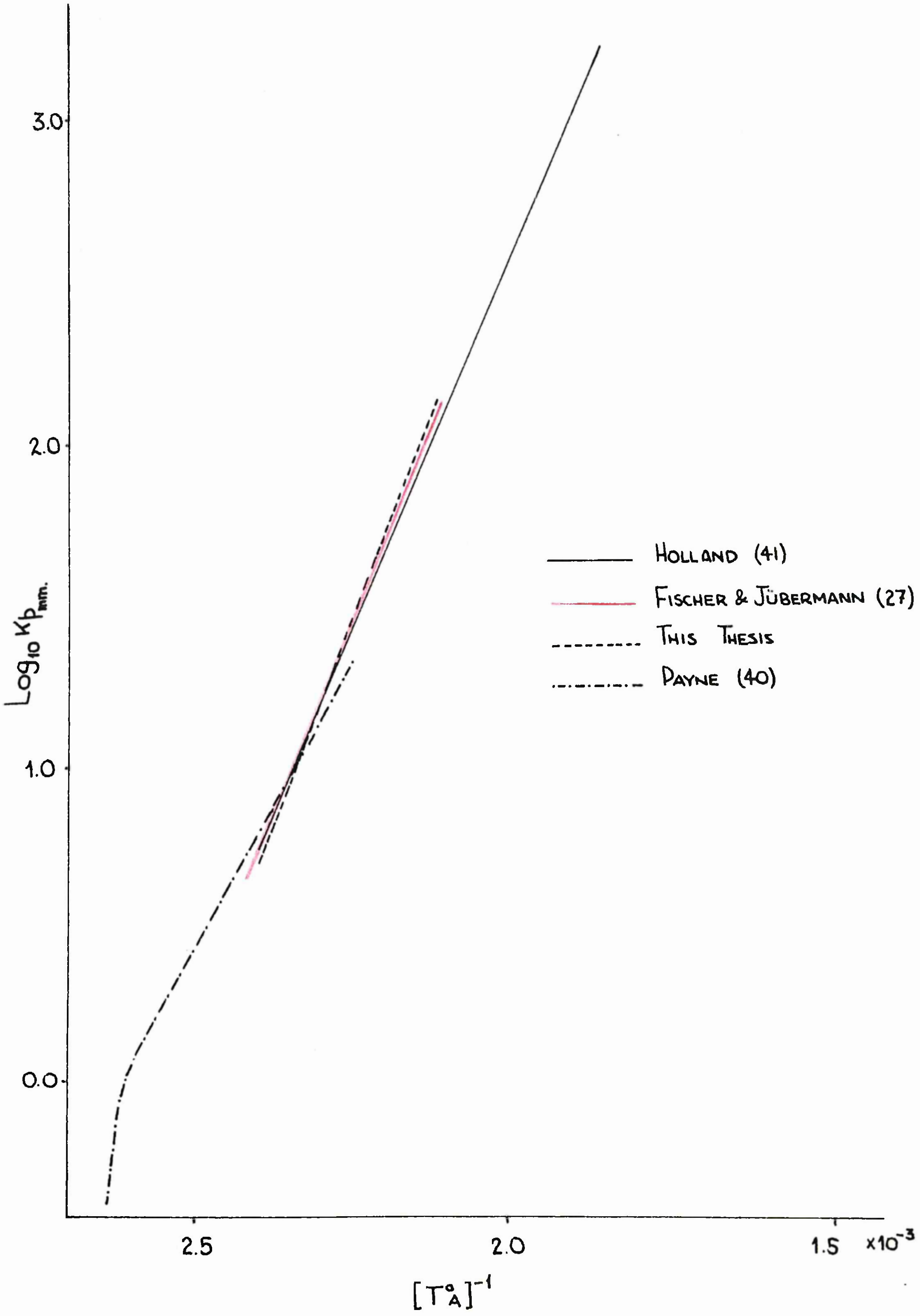
(41)

Table 33c.

Temp °C	$\log_{10}Kp_{mm.}$	Temp °C	$\log_{10}Kp_{mm.}$
149·6	0·79	181·0	1·69
152·8	0·93	184·9	1·75
157·3	1·05	191·5	1·93
169·7	1·22	198·0	1·98
172·3	1·43	200·1	2·12
173·4	1·50	228·9	2·54
		229·2	2·64

(27)

Fig.22. The Vapour Density of Phosphorus Pentachloride.



$[PCl_4^+][PCl_6^-]$ exists but that the system is a polymorphous one, the particular crystalline modification taken up being dependent on the method of preparation and purification adopted. Certainly, the concept of a polymorphous system could adequately explain the variation in vapour pressure reported, and could explain the range of sublimation temperatures which have been found. Further experimental study, focused possibly on the effect of different modes of purification of solid phosphorus pentachloride on the X-ray powder diagrams, is necessary before more definite conclusions can be reached.

EXPERIMENTAL SECTION.

PREPARATIONS.

The Preparation of PF_3Cl_2.

PF_3Cl_2 was prepared by mixing approximately equal volumes of phosphorus trifluoride and chlorine, care being taken to have a slight excess of phosphorus trifluoride in the final mixture, since this can be removed more easily than excess chlorine. The crude PF_3Cl_2 was purified by allowing it to distil slowly, in vacuo, into a trap immersed in a toluene slush bath (-96°) the impurities passing through being condensed in a liquid air trap; twelve to fifteen distillations were required to produce pure material. Apiezon and silicone greases were attacked by PF_3Cl_2; Florube W and Kel-F greases, being the only ones which were stable, were used throughout the work.

Pure samples of PF_3Cl_2 were made immediately before they were required for use; no good method of storing PF_3Cl_2 was found, the most effective was under liquid oxygen.

The Preparation of Phosphorus Trifluoride.

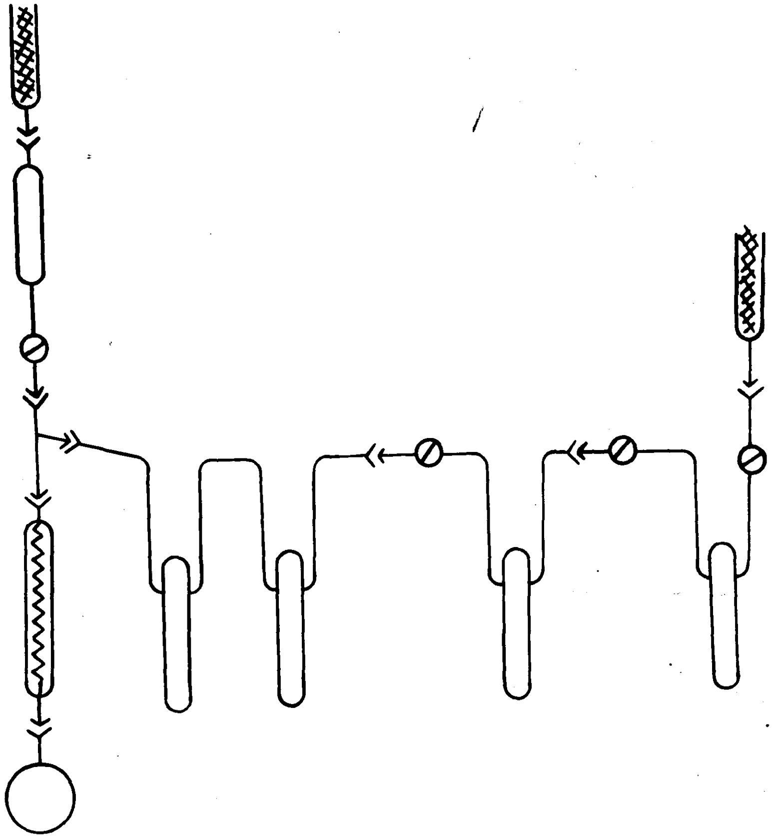
Initially, phosphorus trifluoride was prepared by Hoffman's method (42) viz:

$$PCl_3 + AsF_3 \longrightarrow PF_3 + AsCl_3$$

The apparatus consisted of a glass reaction flask fitted with a dropping funnel and side arm which was connected to a suitable storage vessel. It was found that this preparation was most conveniently carried out on a 0·10 molar scale. The phosphorus trichloride was introduced into the reaction flask and the arsenic trifluoride was allowed to drop in. It was found that the use of antimony pentachloride as catalyst, was unnecessary. The reaction in the absence of catalyst proceeds slowly at room temperature and becomes more rapid with time. The phosphorus trifluoride was used as such, without further purification. The yield over a number of preparations was 70-75%.

It was found that phosphorus trifluoride could be prepared more conveniently by the method of Chatt and Williams (43) using zinc fluoride in place of arsenic trifluoride. The zinc fluoride (B.D.H.) was dried at 140-150° for twenty four hours and phosphorus trichloride (40ml) was dropped slowly at the rate of one drop in three seconds, on to the dry powder (55g). There was an induction period of about five to ten minutes and care was taken not to flood the zinc fluoride thus preventing the reaction from starting. The reaction proceeds briskly at room temperature for about one to two hours. Over the final period it was found necessary to warm the mixture to complete the reaction. The evolved phosphorus trifluoride was purified by passing it through two traps immersed in acetone/drikold mixture (-78°) and condensed in two further traps immersed in liquid oxygen. Since frequent preparations of phosphorus trifluoride were required, an all-glass generator and purification apparatus was built, a diagram of which is reproduced in figure 23. After the evolution of gas had ended tap A was closed and the liquid air bath removed, allowing the gas to distil into the end trap. Tap C was kept open throughout this process; the contents of the traps were protected from moisture and carbon dioxide by a tube containing Sofnolite. When all the phosphorus trifluoride had been condensed in the end

Fig.23. The Phosphorus Trifluoride Generator.



trap, taps B and C were closed and the trap was removed from the system. It was then attached to the vacuum system, evacuated and the liquid air bath was removed, allowing the condensed gas to evaporate into a suitable storage vessel. It was found that phosphorus trifluoride prepared in this way was contaminated by silicon tetrafluoride formed by attack on the glass apparatus by the zinc fluoride. However, since this contaminant could effectively be removed during the purification of PF_3Cl_2, no steps were taken to remove it at this stage.

Several advantages were derived from this method of preparation: large quantities of phosphorus trifluoride could be prepared if necessary and furthermore, use of zinc fluoride dispensed with the necessity of preparing arsenic trifluoride.

The Preparation of Arsenic Trifluoride.

Arsenic trifluoride was prepared by the method described by Hoffman (44) viz:

$$As_2O_3 + 3CaF_2 + 3H_2SO_4 \longrightarrow 2AsF_3 + 3CaSO_4 + 3H_2O.$$

The reaction was carried out in a round bottomed glass flask fitted with a still head, the arm of which was attached to a trap immersed in ice. A thermometer was inserted in the still head; all joints were lightly lubricated with Florube W. grease.

A dried intimate mixture of reagent grade 0·30 mole calcium fluoride and 0·10 mole of arsenious oxide was introduced into the reaction flask. To this 0·95 mole of reagent grade sulphuric acid was slowly added. The apparatus was assembled and the mixture slowly heated over a small bunsen flame to distil the product as formed.

The total distillate was found to be suitable for use in preparing phosphorus trifluoride. Yield over several preparations 70%

Phosphorus Trichloride.

Phosphorus trichloride (Albright and Wilson) was fractionated using a two foot column packed with Fenske rings and the fraction distilling at 74-75° was taken.

Chlorine.

Cylinder chlorine was fractionated in vacuo through a trap maintained at -78° and condensed at -183° ready for use. This process removes traces of moisture ahd hydrogen chloride.

The Preparation of $[PCl_4^+][PF_6^-]$.

Solid $[PCl_4^+][PF_6^-]$ was prepared by controlled fluorination of a solution of phosphorus pentachloride in arsenic trichloride, according to the scheme:

$$[PCl_4^+][PCl_6^-] + 2AsF_3 \longrightarrow [PCl_4^+][PF_6^-] + 2AsCl_3.$$

The method of preparation and the apparatus used are as described by Kolditz (15). Yields over several preparations were theoretical.

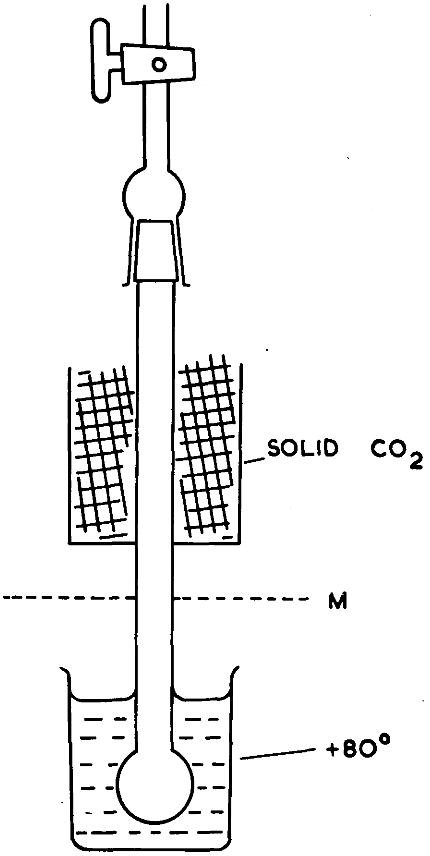
The Preparation of $[PCl_4^+]F^-$.

Attempts were made to prepare $[PCl_4^+]F^-$ by pyrolysis of a $[PCl_4^+][PF_6^-]$ suspension in arsenic trichloride, at 80° according to the scheme:

$$[PCl_4^+][PF_6^-] \longrightarrow [PCl_4^+]F^- + PF_5.$$

The reaction, reported in detail by Kolditz, (16) was carried out in the apparatus described under the preparation of phosphorus trifluoride. Certain modifications were used in an attempt to improve the yields of $[PCl_4^+]F^-$: the glass reaction flask was replaced by a two-necked flask thus allowing a stream of dry nitrogen gas to be passed through the apparatus. This procedure was, however, found to be ineffective and was discontinued. Separation of the mixed solid product obtained in this preparation was attempted by fractional sublimation. A sketch of the sublimation apparatus is shown in figure 24. Essentially, the apparatus consists of a long tube some 30 cm. in length which is attached to the vacuum system. The mixture to be separated is placed in the tube and surrounded by a bath of liquid paraffin maintained at 80°. Sublimation occurs and a solid deposits in the zone cooled by solid carbon dioxide. The tube is then removed to the dry-box

Fig.24. Sublimation Apparatus.



where it is carefully broken at a point M, mid-way between the residue and sublimate.

The Preparation of Pure Ammonia.

Ammonia from a cylinder was treated with metallic sodium in a vessel similar to that described by Sanderson (45). By this procedure any moisture present was converted to sodium hydroxide and hydrogen. The liberated hydrogen was then pumped away and dry ammonia distilled into a storage vessel.

The Preparation of the Nitron Complex with the $[PF_6^-]$ ion.

The preparation is an adaptation of that described by Kolditz (46). The weight of material taken was such as to contain 0·01g. $[PF_6^-]$ ion. The solid was hydrolyzed by 3 ml. of 0·1N sodium hydroxide, acidified with dilute acetic acid and 0·02g. silver acetate added with stirring. The precipitated silver chloride was removed by filtration, and the complex formed by the addition of 0·3g. Nitron reagent (A.R.) in 3 ml. dilute acetic acid to the solution. The complex was then filtered off and dried at 110° in an air oven for three hours.

The Preparation of Ammonium Hexafluorophosphate.

Ammonium hexafluorophosphate was prepared by the action of heat on a mixture of ammonium fluoride and phosphorus pentachloride; the method is fully described by Lange and Kruegar (47). After dissolving the reaction product in water, a solution of Nitron in dilute acetic acid was added and the resulting precipitate filtered. The still damp solid was then separated in a separating funnel with chloroform and 25% ammonia solution, the Nitron reagent being taken up in the organic solvent. The aqueous solution was then evaporated to dryness in a platinum crucible.

The Preparation of Phosphorus Pentafluoride.

Phosphorus pentafluoride was prepared by the reaction between solid phosphorus pentachloride and arsenic trifluoride. The reaction, first observed by Thorpe (48), can be represented thus:

$$3PCl_5 + 5AsF_3 \longrightarrow 5PF_5 + 3AsCl_3.$$

The rate of formation of phosphorus pentafluoride was effectively controlled by the rate at which the arsenic trifluoride was added. The volatile products of reaction were first passed through two traps immersed in Dewar flasks containing an acetone/drikold mixture

(-83°). This procedure effectively removed any reactants carried over in the gas stream. The products were then condensed under liquid air and taken to the vacuum line for further purification. A preliminary I.R. investigation showed the impurities to consist wholly of small amounts of phosphorus oxyfluoride and silicon tetrafluoride. It was found that silicon tetrafluoride and phosphorus pentafluoride could not be separated by fractional condensation since each substance has a boiling point in the range -95° to -100°. However, since the aim of this experiment was to prepare a sample of phosphorus pentafluoride for I.R. study, no attempts were made to separate it from silicon tetrafluoride as the latter substance has but one characteristic frequency (1032 cm.^{-1}) in the I.R. Removal of the last traces of phosphorus oxyfluoride was effected by allowing the impure gaseous mixture to cycle through four traps immersed in toluene slush baths (-96°), five such distillations being required. The 'pure' phosphorus pentafluoride was stored under liquid oxygen until required.

The Preparation of Phosphorus Oxyfluoride.

Phosphorus oxyfluoride was prepared by the action of phosphorus oxychloride on zinc fluoride. Silicon tetrafluoride in large amounts was formed by reaction with the glass apparatus. This contaminant was removed by allowing the impure mixture to pass repeatedly through traps immersed in toluene slush (-96°). After some 10-15 such distillations, the phosphorus oxyfluoride condensate at -96° was found to be pure.

GENERAL TECHNIQUES.

In general halides of phosphorus have the practical disadvantage of being very sensitive to moisture. This effect is very prevalent when dealing with the mixed halides of phosphorus V, especially PF_3Cl_2. Therefore, in order to study these compounds, it was necessary that they should be handled in the absence of water vapour. To this end, a vacuum system was used extensively, providing the best method of working with volatile compounds such as PF_3Cl_2 in the absence of water. In the instance of involatile compounds, particularly solids, the vacuum system was severely limited in its use and a nitrogen-filled dry-box was used to handle these compounds. These special techniques and apparatus which were used are described in the following account.

Vacuum System.

The vacuum line, constructed of Pyrex glass, consisted of a pumping system connected through protective traps to a main line from which branched off various sub-sections concerned with preparation and storage, vapour pressure measurement, pyrolysis, measurement of molecular weight and fractionation. In addition, there were several ground glass joints at various sites in the system, which allowed temporary attachment of apparatus for the study of conductance, sublimation, the introduction of materials, and the admission of dry air. The pumping unit was made up of an Edward's mercury diffusion pump (Type 1M2) backed by a "Metrovac" rotary vacuum pump (Type SR2).

Vacuum taps used in the system were lubricated with Florube "W" and "H", and Kel-F greases; Apiezon and silicone greases were found to be generally unsuitable.

Purification of Volatile Materials in vacuo.

Purification in vacuo was achieved by fractional condensation through a series of U-tube type traps. Traps were maintained at required temperatures by surrounding each one with a Dewar containing a suitable freezing mixture. During the course of the work the following coolants were used: liquid nitrogen -196°, liquid oxygen -183°, iso-pentane slush -160°, toluene slush -96°, acetone and solid carbon dioxide -80°, carbon tetrachloride slush -25°. Intermediate temperatures in the range -80° to +20° were obtained by adding suitable quantities of solid carbon dioxide to an acetone bath.

Hydrolysis.

The hydrolysis of PF_3Cl_2 and other volatile materials was carried out in a bulk of capacity ca.250 ml, fitted with a tap and joint. The material to be hydrolysed was first condensed in an evacuated bulb by surrounding it with a Dewar flask containing liquid air. The cold bath was removed and 50 ml. of 0•5N sodium hydroxide was introduced rapidly into the bulb which was then allowed to stand for about one hour in order that any volatile product of hydrolysis such as hydrogen chloride would be reabsorbed. The hydrolysate was then transferred to a graduated flask and made up to a standard volume with distilled water.

For the hydrolysis of solids, use was made of a small speciman tube (2•5×0•6mm) which was placed inside a stoppered weighing bottle and the whole weighed. This was then taken into the dry-box and the small tube charged with a suitable quantity of the solid material; the weighing bottle and contents were then reweighed and returned to the dry-box. The small tube and contents were then dropped very quickly into a suitable amount of hydrolysing agent, usually 50 ml. 0·5N sodium hydroxide, contained in a flask which was immediately stoppered. The flask and its contents were then allowed to stand for about one hour before the hydrolysate was removed and made up to a standard volume as described above.

The resulting solutions from these procedures were then analysed quantitatively. However, in the case of these solids containing the $[PF_6^-]$ ion an additional procedure was necessary. Due to the resistance of the $[PF_6^-]$ to hydrolysis under the conditions described above, it was found essential to hydrolyse solutions, containing this ion, under more rigorous conditions. To each portion of solution was added an equal volume of concentrated nitric acid and the resulting solution was reduced to small bulk. It was found that after repeating this operation twice, the $[PF_6^-]$ ion was completely hydrolysed and could thus be analysed quantitatively.

Analysis:

Chloride ion in solution was estimated gravimetrically as silver chloride. Phosphorus present as phosphate was first precipitated as ammonium phosphomolybdate. This was then taken up with excess dilute sodium hydroxide and the excess determined with standard acid. Fluoride ion in solution was converted to silicon tetrafluoride by distillation from a perchloric acid solution in the presence of soft glass beads. A known amount of lanthanum nitrate solution was then added to completely precipitate the fluoride and the excess lanthanum determined gravimetrically (49).

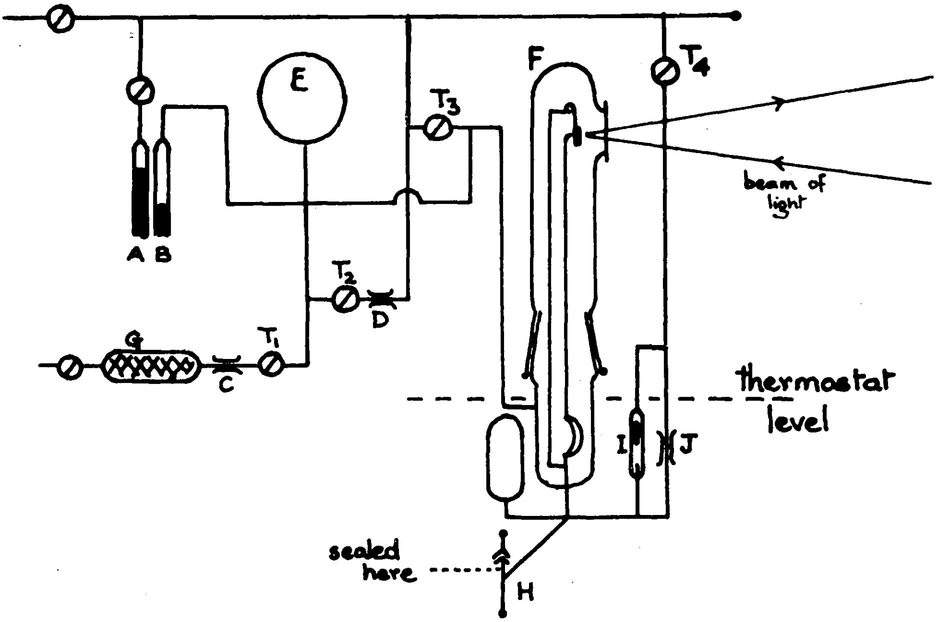
X-ray Powder Photography.

Powder photographs were taken with the "Unicam" powder camera of diameter 11·45 cm. Specimens were contained in sealed Pyrex glass capillary tubes. Very fast, high contrast film (Ilford-Industrial G) was used. The radiation employed was CuK_a and the exposure time of each film was between fifteen and twenty hours.

Vapour Density and Pyrolysis.

The apparatus shown diagrammatically in figure 25 was used for the vapour density measurements of phosphorus pentachloride, $[PCl_4^+][PF_6^-]$, and $[PCl_4^+][PCl_5F^-]$. It was also

Fig.25. Vapour Density and Pyrolysis Apparatus.



found to be suitable for use in the pyrolysis studies of PF_3Cl_2. Initially a spoon gauge was used in the system but this was replaced by a spiral gauge which was found to be more suitable.

Pressure measurements were carried out in the following manner:

The gauge in the system was used as a null instrument in which the deflection of the pointer was magnified by an optical lever system. The small mirror which was actuated by the pointer reflected a parallel beam of light on to a scale at a distance of 1 metre. Calibration of the instrument showed that a pressure differential of 1 mm. of mercury resulted in a deflection of the beam of light of 100 mm. on the scale. It was thus possible to determine accurately the null point of the instrument.

The pressure of the system under investigation was compensated by admitting dry air to the chamber F through the drying tower G and tap T_1. By means of the capillary C and chamber E, it was possible to obtain a high sensitivity for this operation. The pressure in chamber F could be reduced by withdrawing air to the vacuum line by means of tap T_2 and constriction D. Thus when the instrument was adjusted to the null point, the pressure of the system could be obtained from the two wide-bore mercury manometers which were arranged close to each other. Manometer A was used as a barometer and the difference in mercury levels in A and B was read by means of a 0·01 mm. cathetometer.

A good temperature control was obtained using a twenty litre oil thermostat which was heated by two 1000 watt immersion heaters. The thermostat was stirred by two paddle stirrers driven by two Edwards' motors and the temperature was controlled by a Sunvic Thermoregulator (Type TS 2 NC) and Relay (Type F 102/3).

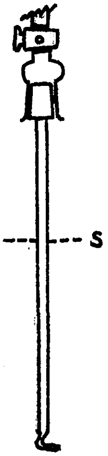
Before the apparatus was used, it was thoroughly baked out to remove traces of water vapour adsorbed on the glass walls. Baking out was effected by maintaining the apparatus at 200° in an air oven and evacuating to a pressure of 10-4 mm. This procedure was continued for 5-6 days.

Samples of volatile material were introduced into the apparatus in the following manner:

A known amount of the volatile compound was condensed in finger H by surrounding it with a liquid air bath. The upper part of finger H was then removed by sealing it at the point shown in the diagram. With taps T_3 and T_4 open, the apparatus was evacuated for ca.30 minutes and following this constriction J was sealed off. The sample was thus contained in an all-glass system of capacity approximately 300 ml.

Solid materials were introduced in the following manner:

A suitable quantity of solid was placed in the ampoule, this operation being carried out in the dry-box. A diagram of the ampoule is shown below. The ampoule was then attached to the vacuum system and the end was immersed in liquid air so as just to cover the solid contents. The ampoule was then evacuated for approximately 1 hour and finally sealed off at the point S and weighed. By weighing the glass fragments obtained at the conclusion of the experiment, the amount of solid used could be carefully

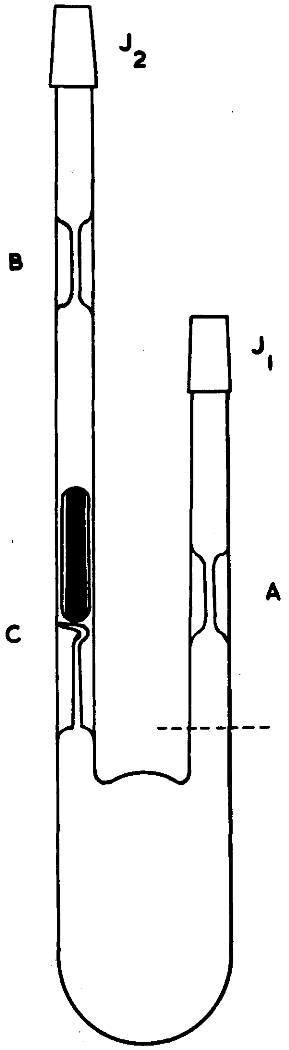


measured. The ampoule and its contents were carefully introduced into finger F with the break seal uppermost. A glass covered metal seal-breaker was next carefully placed above the ampoule by means of a magnet and finger F sealed off as before. After the system had been evacuated as described above constriction J was sealed off. The ampoule was then opened by breaking the seal and the measurement of pressure variation with temperature commenced.

The constant volume part of the apparatus was surrounded by the thermostat tank up to the level indicated. After a complete series of pressure measurements were made for both ascending and descending temperature steps, the experiment was concluded and the products examined. The volatile products were removed by breaking the seal I magnetically, at room temperature and distilling them into a suitable storage vessel.

The capacity of the system was determined by allowing a know volume and pressure of sulphur dioxide to expand within it and measuring the decrease in pressure. This operation was repeated in order to provide a check on the accuracy of the measurement. The volume values obtained

Fig.26. Pyrolysis Vessel.



were found to be reproducible to within 1%.

In order to carry out a detailed examination of the products of the reaction of heat on PF_3Cl_2 a number of pyrolysis experiments were conducted in specially designed vessels. A diagram of one such vessel is shown in figure 26. The apparatus consists of a U-shaped bulb of approximate capacity 50 ml. with two limbs of unequal length fitted with ground glass joints J_1 and J_2. The shorter limb has a constriction A, whilst the longer limb has a constriction B and a magnetic break seal C. The experimental procedure for using the apparatus is as follows; a pure sample of PF_3Cl_2 of known amount was condensed in the bulb by immersing it in a liquid air bath. The bulb was then evacuated and sealed off at A. The cold bath was next removed and the apparatus placed in a heater maintained at a suitable temperature for a suitable period of time. After pyrolysis had been carried out, the apparatus was attached to the vacuum system by joint J_2 and the dead space evacuated. The seal at C was then broken magnetically and the products of pyrolysis separated by allowing the volatile portion to distil into a suitable storage vessel for further examination. The bulb which now contained only the solid product, was sealed off at B until required. The solid product was obtained by taking the bulb into the dry-box and breaking the smaller limbs at a suitable point shown by a dotted line in the diagram. Each experiment was carried out in duplicate.

The heaters used in this study were constructed in the following manner: Each heater consisted of a metal can large enough to contain that volume of the apparatus between the two glass seals. Two cans were connected in series and each was heated by six yards of Nichrome wire (10Ω/yd.) wound onto the walls but separated from the metal by asbestos paper. The heating strip was insulated by a layer of asbestos paper and finally asbestos tape was wound over the paper. The power of each heater thus constructed was 250 watts.

Vapour Pressure Measurement.

The vapour pressure of PF_3Cl_2 was measured by a static method in an all-glass system incorporating a spiral gauge which was used as a null meter. The instrument was accurately adjusted to the balance point by means of an optical lever system. Pressures were obtained as a difference in mercury levels on a wide manometer, a cathetometer being used for accurate measurement.

Temperatures below that of the room were obtained by using a bath consisting of a Dewar flask containing acetone, cooling being achieved by the addition of small pieces of solid carbon dioxide; the bath was warmed by adding suitable amounts of acetone. Satisfactory temperature control was achieved by this method, and a pentane thermometer was used for temperature measurement.

Molecular Weight Determination.

Molecular weights of vapours were measured by weighing the vapour at a known temperature and pressure in a bulb of capacity ca.300 ml. This enabled molecular weights to be calculated with an accuracy of ca.1%.

Melting Point.

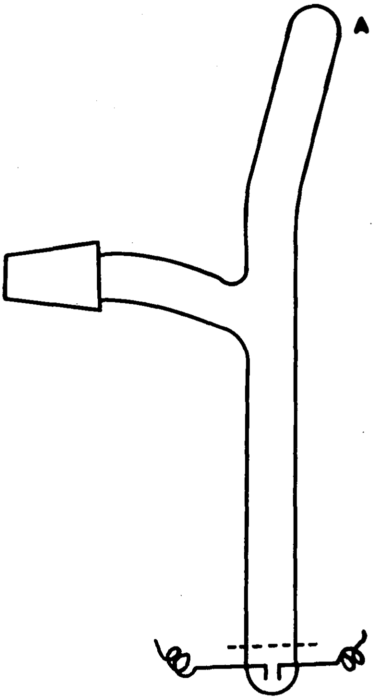
The melting point of solid PF_3Cl_2 was measured by surrounding a sample with an iso-pentane bath (-160·5°) and allowing the bath temperature to rise slowly until the solid appeared just to melt, the procedure being repeated three times to obtain a reproducible melting range.

THE MEASUREMENT OF CONDUCTANCE IN ACETONITRILE.

The conductance of solutions of PF_3Cl_2 in acetonitrile was measured in an all-glass cell fitted with a pair of smooth platinum electrodes (area ca.1cm^2. cell constant 0·324cm.$^{-1}$) and maintained at a constant temperature by means of a water bath. Solutions for conductance measurements were prepared by passing a known weight of pure sample in a slow stream of dry nitrogen into a weighed amount of solvent. The conductance was measured by a Mullard conductance bridge (Type E7566). Readings were taken immediately the PF_3Cl_2 had passed into solution and observations on the variation of bridge reading with time were carried out. The acetonitrile was purified essentially as by Smith and Witten's method (50). However, immediately before use, the solvent was distilled in vacuo from ca.0° to -30°. This procedure served to remove phosphoric oxide, traces of which sublimed over from the desiccating agent during distillation at ordinary pressures. The purified material had a specific conductance of 5×10^{-7} ohm.$^{-1}$cm.$^{-1}$

The conductance of liquid PF_3Cl_2 was measured in an all-glass cell with small platinum electrodes, the cell

Fig.27. Conductance Cell used for Liquid PF_3Cl_2.



specially constructed to deal with small quantities of volatile material. Measurements were made using the Mullard bridge. A diagram of this cell is shown in figure 27. A sample of PF_3Cl_2 was condensed in finger A by surrounding it with a Dewar flask containing liquid oxygen. The liquid oxygen bath is then removed and the cell slowly rotated about the ground glass joint, allowing the liquid PF_3Cl_2 to run down the walls and cover the platinum electrodes to a depth indicated by the chain line.

The conductance of solutions of $[PCl_4^+][PCl_5F^-]$ in acetonitrile were obtained by preparing solutions of suitable concentration in the dry-box and then inserting the dipping electrodes described above. The apparatus was then removed from the dry-box and placed in a beaker of water maintained at 20° and the conductance measured as before.

THE DETERMINATION OF TRANSPORT NUMBERS.

Transport numbers were determined by Hittorf's method which entails the measurement of small changes in the electrolyte concentration which take place at the electrodes, when a solution is electrolysed.

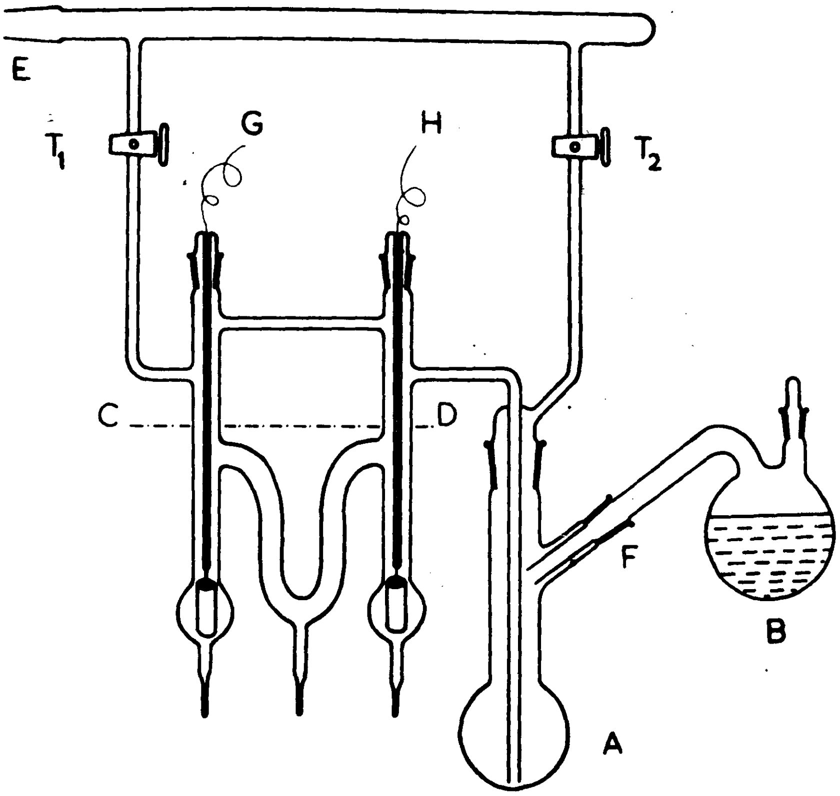
Since the measured changes in concentration are generally small, steps must be taken to minimise the mixing of the anode and cathode solutions. The factors which can cause mixing of the electrode solutions are mainly convection and diffusion. In theory, it is possible to reduce these effects by inserting a sintered glass partition between the electrodes and by increasing the length of the column of solution. These devices however, cause increased resistance to electrolysis and thus smaller concentration changes result.

Transport number determination in systems of mixed phosphorus halides is further complicated by the extreme sensitivity of these compounds to moisture.

It was with these factors in mind that the following electrolysis cell was used.

The cell, which was of the H type with a U-shaped

Fig.28. Electrolysis Cell.



middle compartment, is shown in figure 28. The inner diameter of the compartment was 14 mm. this width being enlarged at the electrodes. This is reported as effectively reducing the cell resistance (52). Since it was considered undesirable to have taps in contact with the solution being electrolysed, easily broken spindles were drawn out as a means of emptying each compartment. The cell could then be emmersed in a thermostat thus off-setting the heating effect induced by electrolysis. Each electrode consisted of smooth, coiled, platinum foil of total surface area 37·5 cm^2. and their distance of separation was 40 cm.

Manipulation of the solution in the apparatus was effected by making use of pressure difference. The experimental procedure in operating the cell is as follows:

Before use the apparatus was attached to the vacuum system at the joint E and flamed out. After allowing dry air to fill the system, flask B was detached and taken into the dry-box.

The solution to be electrolysed was prepared in flask B which was then removed from the dry-box and re-attached to the apparatus. At this stage the main line was evacuated after closing taps T_1 and T_2. The solution was then transferred to flask A by rotating B about the joint F. By opening tap T_1 it was then possible to fill the cell with solution to the mark CD. The cell was then filled with dry air by carefully controlling taps T_1 and T_2 thus making the pressure above the solution, atmospheric. The cell was then immersed in a water thermostat maintained at 20° and the solution was electrolysed by direct current from three high tension batteries, each of capacity 120 volts, connected in series.

When electrolysis was completed, after 90 minutes, the compartments were emptied (middle first) and each solution analysed. The quantity of current used during electrolysis was obtained from the increase in weight of the cathode of a silver coulometer incorporated in the circuit. During electrolysis the current was maintained at 10 m.A.

The design of the silver coulometer was as follows:

A sintered glass crucible (H4) was placed in a beaker (100 ml.) containing silver nitrate solution (10%) such that the crucible was almost filled with solution. The cathode consisted of a platinun electrode (area 1 cm^2.) immersed in the solution inside the crucible.

Before electrolysis, the cathode and crucible were weighed. On completion of the experiment, cathode and crucible were carefully washed with distilled water then acetone and finally dried at 100° in an air oven. The weight of silver deposited was then obtained by reweighing cathode and crucible.

THE REACTION WITH WATER VAPOUR.

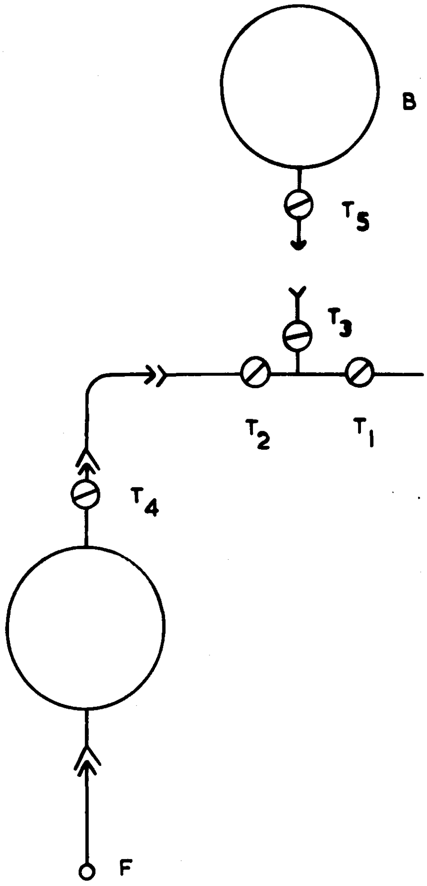
The reaction between PF_3Cl_2 gas and water vapour was carried out at room temperature (20°). A bulb of approximately 300 ml. capacity was filled to the pressure corresponding to the vapour pressure of water at 20°, with PF_3Cl_2. This was then removed, and the bulb refilled with water vapour to the same pressure by allowing it to come to equilibrium with liquid water. The two were then brought into contact and the vapour phases allowed to react, the pressure of the system being observed by means of the spiral gauge system previously described.

The products of the reaction were divided into a volatile and a non-volatile fraction which were hydrolysed with 0·1N sodium hydroxide and the resulting solutions analysed.

THE REACTION WITH AMMONIA.

The reaction between PF_3Cl_2 and ammonia was studied in an apparatus, a diagram of which is shown in figure 27. Initially the molecular weight **bulb** B (capacity ca.300 ml.) was attached to the vacuum line and the system was evacuated for 2-3 hours. Tap T_3 was then closed and bulb B removed to the storage sections of the apparatus where it was filled to a pressure of 700 mm. with pure PF_3Cl_2, the pressure being accurately measured by the spiral gauge system. The bulb B was then re-attached to the apparatus and with tap T_2 closed and T_3 open, the dead space was evacuated. Tap T_1 was closed and the contents of bulb B were condensed in the finger F surrounded by liquid oxygen, by opening tap T_5. On completion of this operation taps T_3 and T_5 were closed and bulb B was removed to the spiral gauge where any residual pressure was measured. This entire procedure was then repeated with bulb B containing dry ammonia at a pressure equal to that of the PF_3Cl_2 taken. Tap T_4 was then closed and the liquid air bath surrounding finger F was replaced by an acetone/drikold bath at a temperature of -60°. This bath was allowed to warm up slowly to -40° over a period of two or three hours thus enabling reaction to take place slowly. Finally the cold bath was removed and the finger F allowed to attain room temperature to ensure complete reaction had taken place. Tap T_4 was then opened and the system filled with dry air. The reaction products were then taken to the dry-box for examination.

Fig.27. The Reaction with Ammonia Apparatus.



SPECTROMETRIC STUDIES.

Mass Spectra.

Mass spectra were obtained by making use of a Metro Vick MS 2 instrument. Measurements were carried out at 15 e.v. in the studies of PF_3Cl_2 and its pyrolysis studies and at 50 e.v. with the compounds $[PCl_4^+][PCl_5F^-]$ and phosphorus pentachloride; a working pressure of 10^{-6} mm. was used.

Gaseous samples were transferred to the instrument by means of thoroughly dried bulbs fitted with magnetic break seals; solid samples were contained in narrow glass tubes fitted with ground glass joints and vacuum taps lubricated with Kel-F high vacuum grease.

I.R. Spectra.

The spectra were studied making use of two instruments when available namely a Unicam double beam instrument (type S.P. 100) in the region 3,700 - 375 $cm.^{-1}$ and a Perkin Elmer model 13 double beam instrument in the region 3,700 - 675 $cm.^{-1}$

Gaseous samples were contained in a stainless steel gas cell of 10 cm. path length, fitted with KBr windows, and of approximate capacity 0·2 l. Solid compounds were examined as mulls with Nujol or hexachlorobutadiene. Nujol was somewhat unsuitable as it was very prone to attack by phosphorus halides in general, while hexachlorobutadiene suffered the disadvantage of having rather a high vapour pressure. It was thus found to be advantageous to prepare mulls and measure their spectra as rapidly as possible.

APPENDIX.

I.R. SPECTRA.

Details of the spectra of the following compounds used in this research and reproductions of the spectra are given in the following pages.

a) Phosphorus pentafluoride at 10 mm. pressure.
b) Phosphorus oxyfluoride at 8 mm. pressure.
c) Silicon tetrafluoride.
d) Nitron reagent as a Nujol mull.
e) Nitron-$[PF_6^-]$ complex as a Nujol mull.
f) Ammonium hexafluorophosphate as a Nujol mull.
g) Phosphorus trifluoride at 10 mm. pressure.

With those compounds, examined as Nujol mulls, the frequencies due to the mulling agent have been omitted. (All data is quoted in $cm.^{-1}$).

a) 535s, 568s, 578s,
590s, 875s, 940s,
950s, 960s, 1025vs.

b) 480s, 875m, 999vs,
1410m, 1425m, 1430m.

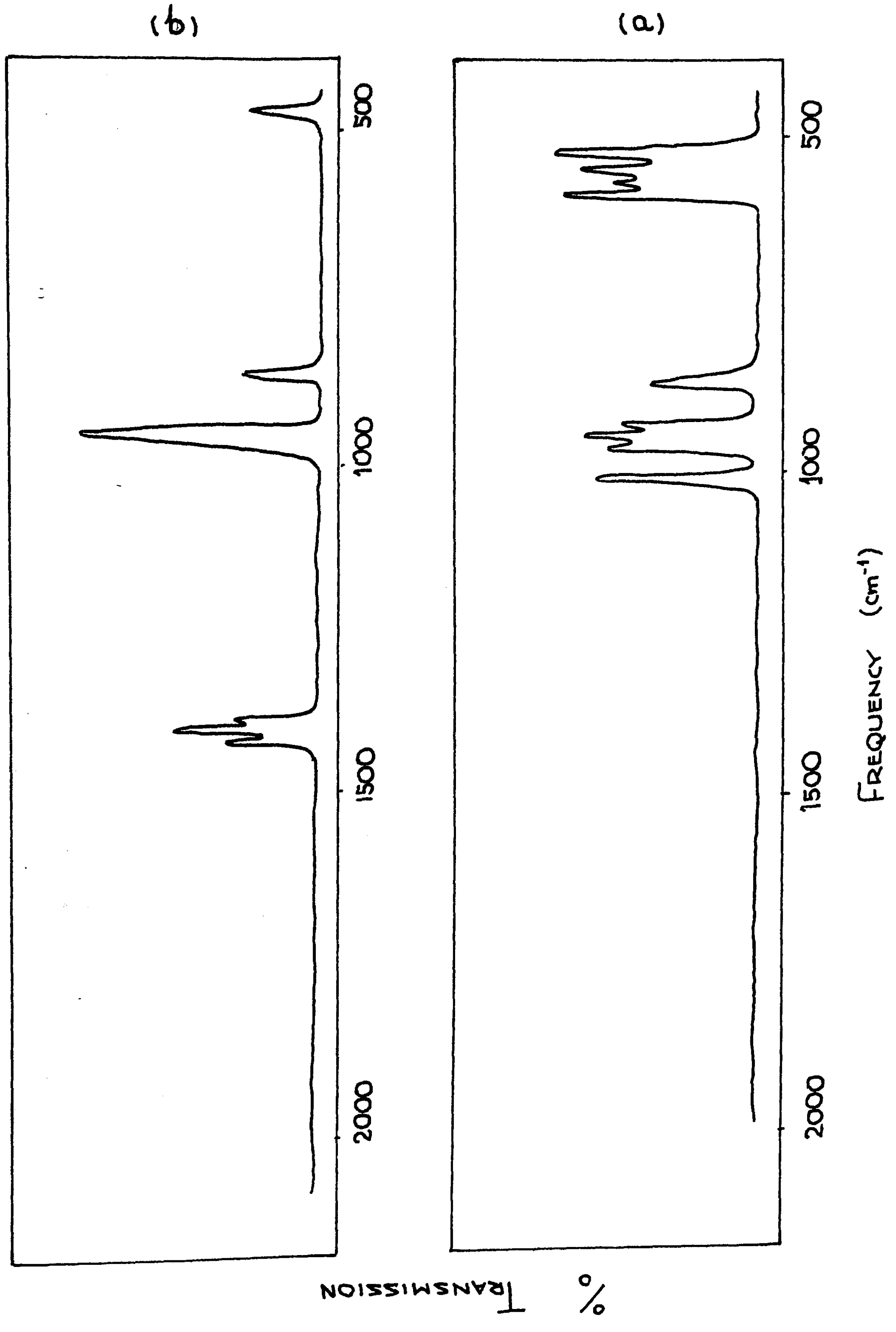
c) 1032vs.

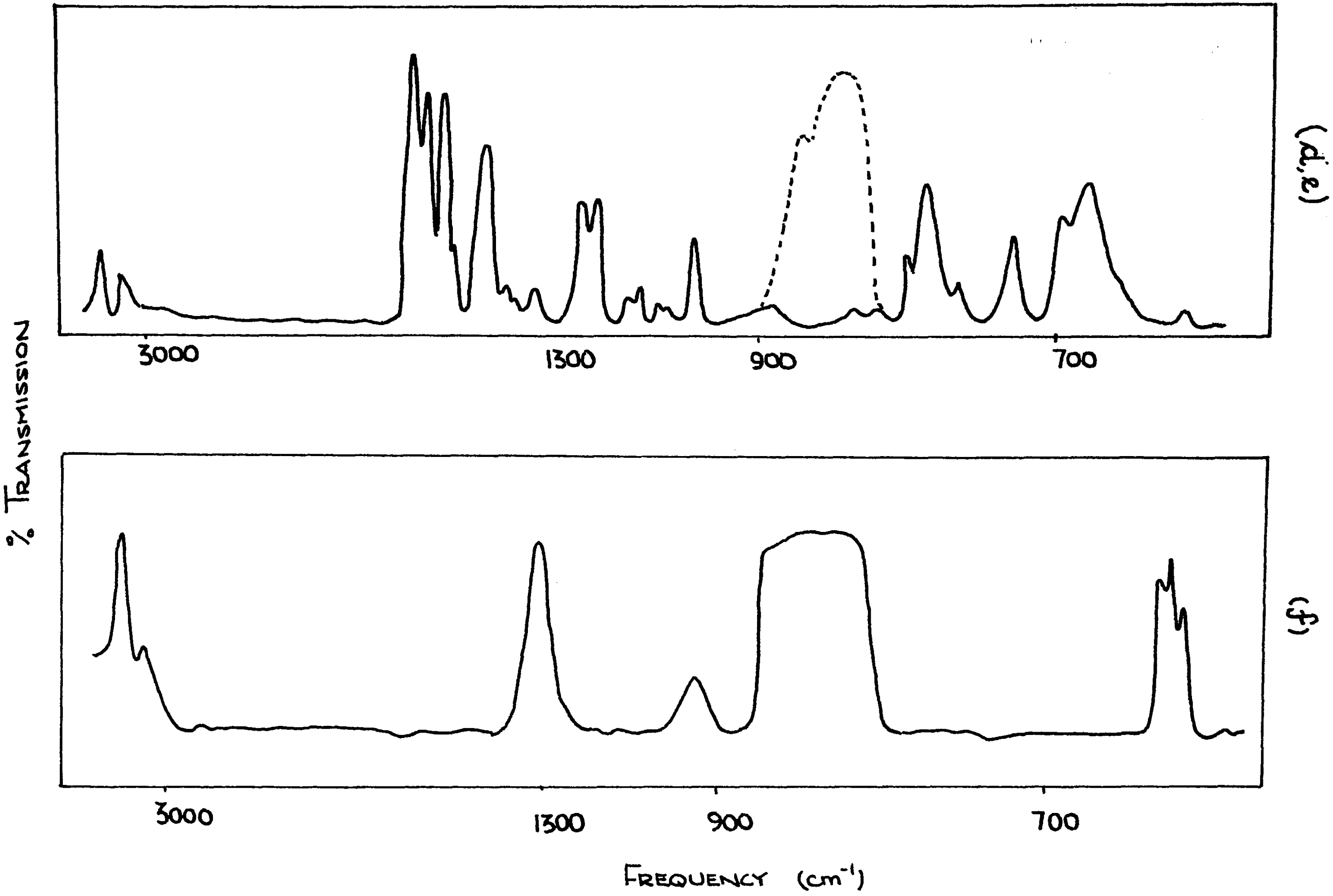
d) 688m, 698m, 712m,
740m, 755s, 777m,
967m, 1008w, 1022w,
1041w, 1063w, 1080w,
1161w, 1214m, 1230m,
1296w, 1338w, 1488s,
1557s, 1593s, 1620s.

e) Spectum d) plus:
820-888 shoulder.

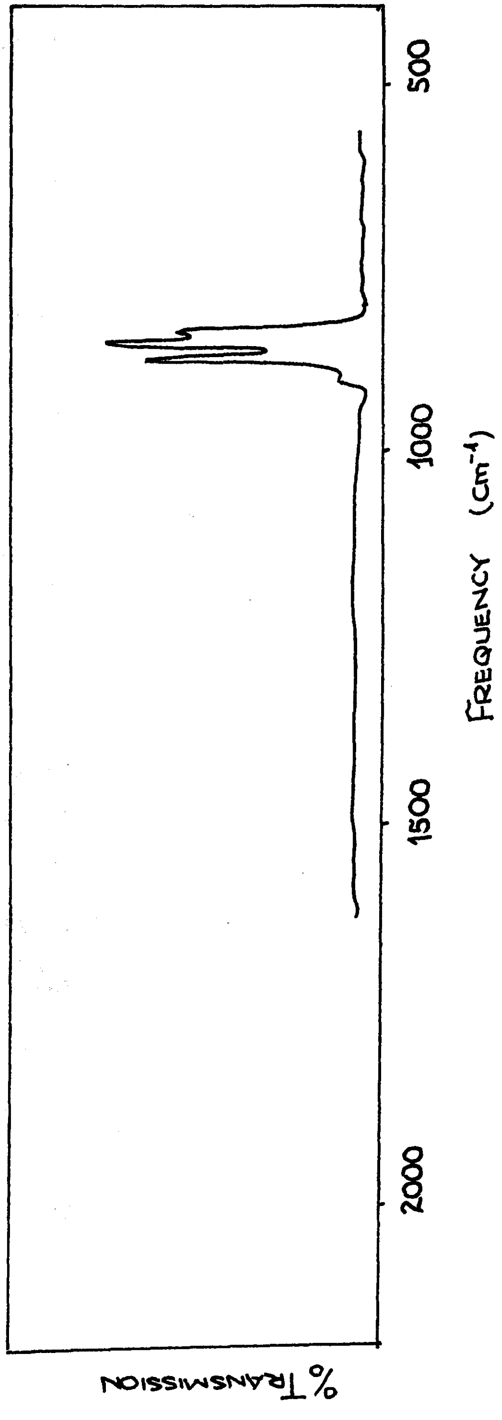
f) 558s, 565s, 570s.
(820-900 shoulder)
1430s, 3350s.

g) 855s, 864s, 894s,
900w.


(b)
(a)
500
1000
1500
2000
FREQUENCY (cm-1)
% TRANSMISSION


(d,e)
(f)
% Transmission
3000
1300
900
700
Frequency (cm⁻¹)

(g)



X-RAY CALCULATION OF d-SPACING.

By a single crystal X-ray study, Clark, Powell and Wells have shown that solid phosphorus pentachloride, purified by recrystallisation from nitrobenzene, has a tetragonal unit cell with a = 9·22 and c = 7·44Å (39). A method of obtaining X-ray powder lines from this work has been evolved and can be illustrated as follows:

Since the unit is tetragonal then a = b and

$$\sin^2\theta = \left(\frac{\lambda^2}{4a^2}\right)h^2 + \left(\frac{\lambda^2}{4b^2}\right)k^2 + \left(\frac{\lambda^2}{4c^2}\right)l^2$$

$$\text{i.e. } \frac{4\sin^2\theta}{\lambda^2} = \left(\frac{1}{a^2}\right)h^2 + \left(\frac{1}{a^2}\right)k^2 + \left(\frac{1}{c^2}\right)l^2 = \frac{1}{d^2_{hkl}}$$

$$\text{and } \frac{1}{a^2} = 1\cdot176 \times 10^{-2} = \frac{1}{b^2}$$

$$\frac{1}{c^2} = 1\cdot807 \times 10^{-2}$$

It is now possible to construct a table of values of the product of the reciprocal of the unit cell dimensions squared and the square of the index term h/l = n, for n = 1 to 7. This is set out in table A.

Now it is most probable that those reflections of high

Table A.

h/1 = n	$n^2/a^2 \times 10^2$	$n^2/c^2 \times 10^2$
1	1·177	1·806
2	4·708	7·224
3	10·59	16·25
4	18·82	28·90
5	29·41	45·15
6	63·72	65·03
7	86·72	88·53

intensity in the single crystal work will give the most important powder lines. Thus applying an arbritary lower limit of 50 to the intensity scale gives some fifteen reflections for h,k, or 1 $\not>$ 7, which will yield powder lines. By using the values of n^2 set out in table A the value of the d-spacing can be obtained.

Example: Selecting the 305 reflection of the hol plane gives:

$$\frac{1}{d^2_{hol}} = (10{\cdot}59 \times 10^{-2}) + (45{\cdot}15 \times 10^{-2})$$

$$\therefore \quad d = 1{\cdot}34\text{Å}.$$

The values of d are set out in table B.

Table B. Calculation of d.

Reflexion	d-spacing Å	Intensity
200	4·61	72
130	2·92	76
400	2·31	60
330	1·93	60
420	2·07	50
150	1·81	50
620	1·21	88
301	2·84	90
103	2·40	62
004	1·86	180
305	1·34	54
005	1·49	69
702	1·03	84
006	1·24	58
107	1·05	56

Very good agreement is found between the calculated values of d and the values quoted in the literature (51).

X-RAY POWDER PHOTOGRAPHS.

X-ray powder photographs of several of the materials used in this thesis were taken and are included here for reference.

The materials studied were

a) Nitron reagent.

b) Nitron-[PF_6^-] complex.

c) Ammonium hexafluorophosphate.

a)

$\theta/_2$	Strength.
4·26	m
4·84	m
5·19	m
5·58	m
6·13	s
6·94	w
7·56	m
8·29	w
8·90	m
9·50	vs
10·25	vs
11·18	m
11·85	s
12·88	s
13·43	m
14·09	m
15·14	w
16·51	w

b)

$\theta/_2$	Strength.
5·15	m
5·94	w
6·54	w
7·40	m
8·83	m
10·00	vs
11·00	s
11·50	m
13·25	w
13·88	w
14·45	s
17·52	w
18·75	w

c)

$\theta/2$	Strength.
8·91	m
9·75	vs
11·25	vs
14·60	m
16·08	s
16·50	s
19·06	s
19·88	s
22·58	w
23·08	w
25·30	m
26·00	m
28·64	s
29·28	w
30·58	w
33·63	s
34·00	w
34·88	s
35·50	s
37·72	m
39·42	w
40·00	w

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