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THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

HIGH PRESSURE SYNTHESIS OF INORGANIC COMPOUNDS

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

EUGENE ALBERT ELPHINGSTONE

Norman, Oklahoma

1972

HIGH PRESSURE SYNTHESIS OF INORGANIC COMPOUNDS

APPROVED BY

Arnold P. Hagen

S. E. Babb, Jr.

H. Feigl

Glenn Dunnhurst

Stanley C. Nyburg

DISSERTATION COMMITTEE

ACKNOWLEDGEMENTS

The author wishes to express his gratitude to his research advisor, Dr. A. P. Hagen, for his patient counsel and support during this investigation.

Acknowledgement is made to the Oklahoma University Department of Chemistry for teaching assistantships and to the National Science Foundation (GP - 19873) for financial support.

Special thanks are extended to my fellow colleagues for their moral support and fraternalism.

Finally, I would like to express my love to the three most important women in my life; my mother, my wife, Frances and most recently, my daughter, Valerie.

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CHAPTER I

INTRODUCTION

The objective of this research was to study the use of high pressure and its influence in inorganic and organometallic synthesis.

The chief systems chosen for detailed study include reac on of three different phase pairs. The transition metal oxide phosphorus trifluoride system studies gas-solid interactions at high pressure. The phosphorus trifluoride - Group VIA elements system combines gas-gas with gas-solid interactions at high pressure. The final high pressure system, the hydrolysis of fluorochloromethanes, involves gas-gas and gas-liquid interactions and is perhaps the most unusual pressure system.

The final study deals with the photochemical substitution of PF_3 for CO on $Cl_3Si\text{-}Co(CO)_4$ under an autogenous pressure of 40 atmospheres of PF_3. This gas-liquid substitution reaction represents a preliminary study to show the use of photochemical substitution in inorganic-organometallic systems where thermal substitution has not been successful.

The first section gives a detailed discussion of the expected influences of pressure on chemical systems.

A. Chemical Reactions at High Pressure.

The following discussion is a qualitative analysis of the effects of high pressure on chemical reactions in the liquid and gas phases.

As stated by Dodge[41] in "High Pressure Physics and Chemistry", "the rigorous calculation of the effect of pressure is rather impractical at the present time, primarily for two reasons: (1) the necessary P,V,T,Y (mole fraction) data are not available for any system and (2) the calculation would be an exceedingly tedious one assuming the data were available".

1. General Thermodynamic Relationships. It will be most instructive to begin with the basic thermodynamic differential energy expressions[127],

$$dE = Tds - PdV \tag{1}$$

$$dH = TdS + VdP \tag{2}$$

$$dG = -SdT + VdP \tag{3}$$

As all the quantities are state functions and are therefore perfect differentials, we can select the differential that will be most instructive in interpreting the effect of pressure on a chemical reaction. That relationship will be the change of G (Gibbs free energy) with pressure at constant temperature, as

$$\left(\frac{\partial G}{\partial P}\right)_T = V \tag{4}$$

If we define a new free energy term as the "partial molal free energy"[127] such that,

$$\left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j} = \bar{G}_i \tag{5}$$

where P = pressure, T = temperature and n_i = moles of component (i) and $n_i \neq n_j$, then we can take the derivative of the partial molal free energy with respect to pressure at constant temperature and composition,

$$\left(\frac{\partial \bar{G}_i}{\partial P}\right) = \frac{\partial}{\partial P}\left(\frac{\partial G}{\partial n_i}\right) = \frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial P}\right)_T = \frac{\partial}{\partial n_i}(V) = \bar{V}_i \qquad (6)$$

where we have used the fact that the order of differentiation is immaterial and have omitted subscripts indicating composition variables held constant. We have now defined a new term, the "partial molal volume", which is the measure of the rate of change of partial molal free energy.

The physical meaning of the partial molal quantities can best be visualized by using the volume as an example. The derivative $(\partial V/\partial n_i) = \bar{V}_i$ is the rate of change of the total volume of the solution (gas or liquid) with the amount of component (i). For example, if we start with a large amount of the solution, the $\bar{V}_i$ is equal to the increase or decrease in its volume when one mole of substance (i) is added. It is worth noting that $\bar{V}_i$ can be positive or negative.

The partial molal volume, an experimentally measurable quantity can then be used to predict the influence of pressure on a chemical reaction. Partial molal volumes are expressed in units of (cm^3/mole) which refers to the volume change of 1 Kg of solution when 1 mole of component (i) is added. Numerical values for $\bar{V}_i$ are commonly in the range of -25 cm^3/mole to (+) 25 cm^3/mole.

In equation 5, the partial molal free energy is in addition to the normal free energy of the system, i.e.

$$dG = SdT + VdP + \sum_i \bar{G}_i \, dn_i \qquad (7)$$

For solutions the partial molal free energy is also the chemical potential,

$$\mu_i = \bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j} \tag{8}$$

In classical thermodynamics a negative ΔG° for a chemical reaction indicates a spontaneous reaction (thermodynamically) and a positive ΔG° indicates a non-spontaneous reaction. From the relationship, $(\partial \bar{G}_i/\partial P)_T = \bar{V}_i$ a negative partial molal volume would give a negative partial molal free energy and a more negative overall ΔG thus making the corresponding reaction more favorable. A positive partial molal volume would give a positive partial molal free energy and a more positive overall ΔG making the corresponding reaction less favorable.

2. Gas Phase Reactions. A detailed discussion of the influence of high pressure on gas phase reactions is presented by Dodge[41] with emphasis on an engineering, or applications point of view. This presentation will be limited to the qualitative considerations of gas phase reactions at elevated pressure.

The classic example of the ammonia-synthesis reaction will illustrate the principles involved.

At 25° and one atmosphere the reaction mixture of N_2 and H_2 is thermodynamically unstable, viz.

$$N_2 + 3H_2 = 2NH_3 \tag{9}$$

Using standard themodynamic tables,[144] an ΔG° of -8.0 Kcal/mole can be calculated for the reaction. Relating ΔG° to the equilibrium constant

$$\Delta G^\circ = -nRT\ln K \tag{10}$$

$$\text{where} \quad K = \frac{[NH_3]^2}{[N_2][H_2]^3} \tag{11}$$

the equilibrium concentration of NH_3 should be 94 mole %. However, this is not so; no apparent formation of NH_3 can be detected, even after long periods of time. In this reaction then, it is kinetic or rate considerations and not equilibrium or thermodynamic considerations which control the reaction. The usual method of increasing the rate is to increase the temperature or employ a catalyst or both. No reasonable amount of pressure increase will do any good, short of pressures high enough to affect the kinetic energy of the valence electrons. If the temperature is raised to 450° with the pressure of 1 atmosphere and a catalyst is added that is known to promote this reaction, very little reaction takes place, just as before. With sufficient thermal energy to react, the reaction is now equilibrium controlled. Finally, the factor of pressure can be brought into action and the concentration of NH_3 increase rapidly as pressure increases. A study by Comings[38] shows that the optimum pressure and temperature are 1000 atmospheres and 200° producing about 97% conversion to NH_3.

It is worth emphasizing that what is actually observed in any chemical reaction is a result of the interplay of the two factors of rate and equilibrium and, in order to interpret observed results correctly, the equilibrium point must be known. Fortunately, this can be rigorously calculated with thermodynamics and does not involve doubtful assumptions except as they may be made because of the lack of necessary thermal and compressibility data.

In general, a reaction in the gas phase is pressure favored if a decrease in volume occurs. Pressure can generally only increase the rate of a reaction in the gas phase by increasing the concentration

of the reactants. The equilibrium constant of the reaction is a function of the thermodynamics of the overall reaction.

3. Reactions Having Condensed Phases. Several detailed discussions are available on the effect of high pressure on reactions having condensed phases. S. D. Hamann[63] has an extensive discussion on both chemical equilibria in condensed phases and chemical kinetics, in general, at high pressure. W. J. le Noble[89] has recently reviewed reactions in solutions under pressure with primary emphasis on organic systems.

In general, transition state theory of reaction rates is the better suited theory for analysis of the role of pressure in chemical kinetics in solution.

Different authors use different notation in their discussion of the theory of reactions in solution at high pressure. The notation used by le Noble[89] will be followed in this text.

In transition state theory it is assumed that the major limitation on a reaction is the rate of formation of an activated intermediate or so called transition state. The same principle applies at high pressure with the added consideration that the volume of the products should be less than that of the reactants so that pressure doesn't retard the rate of formation of products.

Using transition state theory, a reaction of the general type

$$aA + bB + \cdots \rightarrow X^{*} \rightarrow lL + mM + \cdots \qquad (12)$$

where X^{*} is a definite molecular species in equilibrium with the reactants and products. Using this assumption, it is possible to separate the factors constituting a rate constant into kinetic and thermodynamic

terms. In this way, Glasstone, Laidler and Eyring[53] derived the relation

$$k = K \frac{k_B T}{h}(K^*) \tag{13}$$

where k is the specific rate constant, k_B is Boltzmann's constant, h is Planck's constant and K is a factor, close to unity, which defines the probability that the transition state X^* will decompose into the products rather than the reactants. The quantity K^* is defined by

$$K^* = \frac{[X^*]}{[A]^a[B]^b} \tag{14}$$

where [] denote concentration not activity. K^* is then the equilibrium product for the formation of the transition state, uncorrected by activity coefficients. It is important that k and K^* must be based on the same concentration scale.

If it is now assumed that the ratio of conversion to products from the transition state (K) is independent of the temperature and the pressure[49], a new relationship can be developed, where

$$\ln k = \ln K^* + \ln T + \ln(\frac{Kk_B}{h}) \tag{15}$$

such that

$$\frac{\partial(\ln K)}{\partial P} = \frac{\partial(\ln K^*)}{\partial P} \tag{16}$$

In applications at high pressure the derivative assumes a form[63] to account for the compressibility of the solvent as well as the partial molal volume, such that

$$\frac{\partial(RT\ln k_c)}{\partial P} = -(\Delta\bar{V}^*)^\infty + (1-a-b-\cdots)RTk_s \tag{17}$$

where $\overline{V}^* = \overline{V}_X^* - a\overline{V}_A - b\overline{V}_B$, and k_s denotes the compressibility coefficient of the solvent. As Guggenheim[57] has pointed out, only for a first order reaction where a = 1, b,c, ... = 0 in the rate determining step does the second term drop out. It has remained common practice to ignore the second term on the right side of the equation yielding the assumed relationship,

$$\frac{\partial(RT\ln k_c)}{\partial P} = -\Delta V^* \qquad (18)$$

which interprets the influence of pressure on k_c by the excess in partial molal volume of transition state over the partial molal volume of the initial species.

The quantity ΔV^* is usually called a "volume of activation" although it is clearly a composite function. The only justification for identifying it with $(\Delta\overline{V}^*)^\infty$ lies in the fact that the errors involved in measuring rate constants under pressure are sufficient to introduce an uncertainty of a few cm^3/mole into ΔV^* and this is usually greater than the factor RT k_s.

In actual practice, ΔV^* is not independent of pressure and its interpretation is not straightforward. Thus, tabulated values of ΔV^* can be at almost any specified pressure. For comparison purposes, most chemists have adopted the practice of limiting their considerations to ΔV_o^* which is the value of ΔV^* at zero pressure, which for all intents and purposes is the same as the value at one atmosphere.

The value of ΔV_o^* can be estimated by extrapolating the plot of ln k vs P to zero pressure following the general curvature of the higher pressure points. The slope of the curve at zero pressure is

equal to $\Delta V_o^*/RT$. Hyne[76] has investigated the problem of fitting the data to a curve and has concluded that a parabolic expression fits the data best, viz.

$$\ln k = a + bp + cp^2 \qquad (19)$$

le Noble[89] has tabulated estimated values for the partial molal volume of the transition state for various mechanistic features in the rate determining step at zero pressure (ΔV_o^*). Table I lists le Noble's estimates.

A short discussion of the contribution of each mechanistic feature and its contribution to ΔV_o^* will explain the significance of the values.

(A) Bond Cleavage. This refers to cleavage in a covalent fashion to yield two neutral species. As expected, the transition state will contain a bond stretching intermediate and thus a slightly positive (+10) ΔV_o^*.

(B) Bond Deformation. Most of the reported work has been on racemizations. As expected with an intramolecular rearrangement there is very little volume increase ($\sim$0) in the transition state.

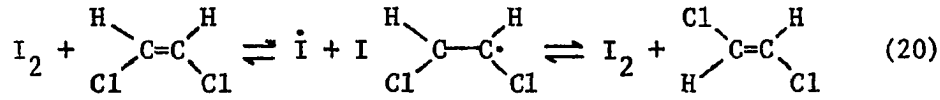
(C) Bond Formation with Neutral Species. An example of this type of reaction (other than polymerizations) would be the Diels-Alder type. With the combination of two molecules or radicals to form one there is a significant negative ΔV_o^* (-25).

(D) Displacement Reactions Involving Neutral Molecules. The reactions involved here include mostly free radical intermediates. One typical example might be the iodine-catalyzed equilibrium of cis- and trans-1,2-dichloroethene.

TABLE I

Factors in Estimation of ΔV_o^*

Mechanistic Feature	Contribution, cm^3/mole
Bond Cleavage	+10
Bond Deformation	0
Bond Formation	-10
Displacement	- 5
Diffusion Control	+20
Cyclization	0
Ionization	-20
Steric Hindrance	- 0
Neutralization	+20
Charge Dispersal	+ 5
Charge Concentration	- 5



(20)

The reaction should depend upon the formation of I· with the net activation volume being slightly positive. Polar additions are characterized by much larger ΔV_o^* (-10)[48].

(E) Diffusion Control. This problem is only apparent at very high pressures for liquid phase reactions. At these pressures some solvents become "glassy" where diffusion of the reactants is slower than the rate determining step. The pressure must usually be in the 30 to 40 thousand atmosphere range with large values of ΔV_o^* (> +20).

(F) Cyclization. This mechanistic feature is particularly important to organic chemistry where ΔV_o^* is as high as +20 cm^3/mole. In general this is thought to be because the small rings don't intertwine so that the ring center is dead volume.

(G) Ionization. Ionization is one of the most mechanistically favored features at high pressure. Since the process implies bond fission, it might be expected that a positive value of ΔV_o^* would follow. However, the simultaneous appearance of a pair of charges alters this interpretation. Each of the charges exerts a powerful attractive force on nearby polar or polarizible solvent molecules resulting in the density in the immediate neighborhood of ions is appreciably higher than in the bulk solvent. The volume decrease on ionization is referred to as electrostriction[42].

For weak acids the value of ΔV_o^* is always negative and in the order of -15 cm^3/mole. It is an interesting phenomenon that ΔV_o^* for

weak bases in water averages about -25 cm^3/mole. The exact explanation is still in doubt.

There are exceptions to the above trend. Carbonic acid[46] and sulfurous acid[47] have unusually large volumes of ionization (-27 and -20 cm^3/mole, respectively). The explanation given attributes the large values to two equilibria occurring, that of hydration and ionization, both of which involve volume decreases, viz.

$$H_2O + CO_2 \rightleftharpoons H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^- \qquad (21)$$

In summary, for many solvolysis reactions, ΔV_o^* tends to be rather large, of the order of -15 to -20 cm^3/mole.

(H) Ionization with Bond Formation. As in the previous paragraphs, ionization contributes to a large negative ΔV_o^*. When two neutral species react to form ionic and covalent products, the value of ΔV_o^* should still be a large negative number.

(I) Ionization with Displacement. Ionization with displacement refers to reactions where two species react to form an ionic product with some atomic displacement. An example would be the reaction of an amine with a substance containing an acidic proton yielding an amine salt. With ionic products this reaction should be highly pressure favored with ΔV_o^* values in the range of -20 cm^3/mole and greater. The studies on this type of reaction[126] indicate that the development of charges in the transition state invariably causes pressure to increase the rate of reaction. For halogens, le Noble summarizes that where the appropriate data are available, the activation volume becomes more negative the smaller the atom, which shows that the incipient negative charge is located there.

(J) Steric Hindrance. There is some indication that pressure can overcome steric hindrance at reaction sites. The argument most elegantly presented by Gonikberg, Zhulin and El'yanov[54] is that "if in a given transition state the reacting sites have been able to get together only at the cost of interpenetration of several interfering groups, its molar volume will be smaller than it would otherwise be, and such reactions are of course accelerated more (or retarded less) than unhindered reactions".

(K) Reactions Dependent on Prior Ionization. These reactions should and generally do proceed with negative activation volumes ΔV_o^* (-20). There is a coupled effect, one of the ionization and then a further decrease due to bonding.

Nozaki[121] has studied the catalyzed isomerization of diethyl maleate which is second order in secondary amine (catalyst). The volume change is for the process,

$$2\ Et_2NH + Et_2(Mal) \rightarrow [Et_2\overset{\delta-}{N}H\text{--------}Et_2(Mal)\text{----}HN\overset{\delta+}{E}t_2] \qquad (22)$$

The large, negative value of ΔV_o^* (-25) is in qualitative agreement with the formation of this dipolar, compact transition state.

(L) Neutralization Reactions. As might be expected, neutralization reactions being just the opposite of ionization reactions contribute to a positive ΔV_o^* (+5). It is not as large as the self-ionization reaction because there are ions remaining in solution (acid + base $\rightarrow$ H_2O + "a salt").

(M) Charge Dispersal. When an ionic substance is quite large such that the charge can be distributed over several atoms, it is found

that there is a much smaller ΔV_o^* (+5) on ionization. This is generally attributed to the spreading out of the polar or polarizible solvent molecules resulting in little or no significant increase in solvent density around the delocalized ion.

(N) Charge Concentration. If on the other hand a large ion breaks apart to yield a neutral species and a small ion, this should result in a slight decrease in the volume such that ΔV_o^* should be slightly negative.

Although there are exceptions to the above arguments presented by le Noble, they can be used to estimate values of ΔV_o^* or to estimate mechanistic features of known reactions.

B. Phosphorus Trifluoride.

Preparation. Moissan[94] first prepared PF_3 in 1884 by the reaction of Cu_3P_2 with PbF_2. Later syntheses involved PbF_2 and P(red)[95] and AsF_3 with PCl_3[104]. Zinc fluoride was employed in the fluorination of PBr_3[96] and PCl_3[177]. Silver fluoride was also used in the fluorination of PCl_3[100].

Most of the metathetical reactions on PCl_3 are of a general nature and can be used for the fluorination of other phosphorus halides. Typical fluorinating agents include SbF_3, CaF_2 and NH_4F at room temperature under autogenous pressure, viz.

$$PCl_3 + SbF_3 \rightarrow PF_3 + SbCl_3 \quad ^{22} \tag{23}$$

$$PCl_3 + CaF_2 \rightarrow PF_3 + CaCl_2 \quad ^{22, 115} \tag{24}$$

$$PCl_3 + NH_4F \rightarrow PF_3 + NH_4Cl \quad ^{175} \tag{25}$$

Other fluorinating reagents include potassium fluorosulfinate[142,143], benzoyl fluoride[139], NaF in tetramethylene sulfone[165], HF[87] (effective at room temperature without a catalyst) and molten alkali or alkaline earth metal fluorides[155,156].

The above methods represent useful syntheses of PF_3, but PF_3 is also observed as a product of numerous reactions involving phosphorus and fluorine compounds. Some examples include the reaction of SbF_5 with PCl_3[138], the reaction of P_2O_5 with CaF_2[158] and the reaction of $NOSO_2F$ and PCl_3. Phosphorus trifluoride was observed as a decomposition product of the adducts of trialkylphosphites with BF_3[103]. Five percent PF_3 was observed from heating P(red) and HF[116]. A migration of fluorine from C to P was observed in the pyrolysis of $(CF_3)_2POP(CF_3)_2$(250°/14 days)[56]. The reaction of $P(N(CH_3)_2)_3$ and BF_3[74] gave PF_3 in a 91% yield. The reaction of excess PCl_3 and MoF_6 formed PF_3[122] and it was claimed to be formed in the electrolytic synthesis of Mn where manganese oxides are dissolved in molten CaF_2 and the carbon anode is converted into CF_4. It was proposed that the CF_4 then reacted with phosphorus or phosphide contaminants yielding PF_3[146].

Chemical Properties of PF_3. PF_3 is a colorless, non-combustable gas of low boiling point (-101°). It is highly toxic and odorless in toxic conditions, if in a very pure state, but has a penetrating, musty odor at high concentrations.

PF_3 is reported not to attack glass at room temperature but at 500° a reaction is observed, viz.[22,96,146].

$$4\ PF_3 + 3\ SiO_2 \rightarrow 2\ P_2O_3 + 3\ SiF_4 \qquad (26)$$

The P-F bond is much stronger than the P-Cl bond as indicated by

the heats of formation of PF_3[168] and PCl_3[73] at -189 kcal/mole and -73.22 kcal/mole respectively.

Hydrolysis of PF_3 is quite slow, so much so that it can be bubbled through ice water without significant decomposition in its preparation and purification[12]. However, hydrolysis of PF_3 does occur rapidly in the presence of an aqueous alkali[115], viz.

$$PF_3 + 6\ NaOH \rightarrow 3\ NaF + Na_3PO_3 + 3\ H_2O \qquad (27)$$

PF_3 is readily oxidized by elemental halogens, reacting with fluorine, viz.

$$PF_3 + F_2 \rightarrow PF_5 \quad [102, 97] \qquad (28)$$

to give a yellow flame of moderate temperature, and reacting with chlorine, viz.

$$PF_3 + Cl_2 \rightarrow PF_3Cl_2 \qquad (29)$$

which according to a recent kinetic study[178] reaches completion at 0° as the reactants warm from -196°.

There has been very little success using PF_3 as an acceptor molecule. For example, no combination occurred[182] when PF_3 was passed over KF in vacuo up to 240°. Some slight absorption is observed at 150°[182].

The donor properties of PF_3, especially towards transition metals, attributes to an unusually stable adduct. This series of compounds will be discussed in the section on transition metal coordination complexes of PF_3.

C. Phosphoryl Fluoride.

Preparation. Phosphoryl fluoride was first mentioned as a product of the interaction of various metal fluorides with P_4O_{10}[151]. A more

detailed report[161] described the formation of OPF_3 upon heating cryolite and P_4O_{10}. Heating P_4O_{10} and CaF_2 at 500°[158] yields OPF_3 in preference to the expected PF_5. Small quantities of OPF_3 were found by heating P_4O_{10} with rock phosphate and with fluoroapatite at 700°, and by heating mixtures of P_4O_{10}, NaCl and CaF_2[158,88]. Sulfur tetrafluoride was employed as a fluorinating agent for P_4O_{10} to yield OPF_3[124] (at elevated temperature under autogenous pressure and in a flow system).

Moissan first recognized that P_4O_{10} could not be used to dry HF because of the formation of OPF_3[101,108]. Likewise, IF_5 reacts with P_4O_{10} to yield OPF_3[13], which forms a weak adduct ($IF_5 \cdot OPF_3$) in solution.

As in the synthesis of PF_3, there is particular importance in the metathetical reactions of the other phosphoryl halides (Br or Cl). Different degrees of fluorination can be obtained under different reaction conditions. Examples of fluorinating agents that can be used include (for $OPCl_3$) ZnF_2[98], PbF_2[58], SbF_3[26], CaF_2[24] at 200° (90%), AgF[100], HF[174] at 65° ($SbCl_5$ - catalyst), potassium fluorosulfinate[143], benzoyl fluoride[139] and NaF in tetramethylene sulfone[164,163,165]. The formation of OPF_3 has also been observed in the reaction of NOF[15], HSO_3[66] and F_2[97] with P_4O_{10}. Other unusual syntheses are the reaction of PCl_5 and HSO_3[67], the reaction of $RCON{=}PCl_3$ and AgF[128], the reaction of $(FSO_2O)_2$ and PF_3[152] and the partial hydrolysis of PF_3Cl_2.

From solid-solid reactions, OPF_3 is obtained upon formation of fluoroapatite from tertiary calcium phsophate, calcium metaphosphate or calcium diphosphate and CaF_2 at elevated temperature (300° → 900°)[18,33,111,110,93]. Strontium phosphate and SrF_2 react analogously[169]. Sodium metaphosphate heated with certain fluorides or fluoroapatite[169]

also yeilds OPF_3.

Berak and Tomczak[19] determined in the thermal analysis of the $Mg_2P_2O_7$ - MgF_2 system that OPF_3 forms from the solid phase reaction above 750°. This reaction is a typical example of an industrial approach to the synthesis of OPF_3.

The above synthetic methods of preparing OPF_3 have not included any oxidation-reduction reactions, a capability phosphorus exhibits by its two stable oxidation states, P(III) and P(V). Several such syntheses have been studied. In 1963, Streng[154] reported the reaction of O_2F_2 and PF_3 at -148° producing PF_5 and polymeric $(OPF_2)_n$ which slowly decomposes at room temperature to give OPF_3. Moissan[106] reported that PF_3 and O_2 reacted on a heated Pt sponge to form OPF_3. Several authors[106,44,103,109,94] reported in the old literature that PF_3 and O_2 detonate upon electric discharge to yield OPF_3. Wannagat and Rademachers[171] have shown recently that PF_3 and O_2 react in a silent electrical discharge, without detonation, to yield complicated P-O-F products with little OPF_3. Hagen and MacDiarmid[61] have shown that PF_3 and P_4O_{10} react at 4000 atmospheres and 250° to give quantitative OPF_3.

Chemical Properties of OPF_3. OPF_3 is a colorless gas of penetrating odor which does not attack glass in the absence of H_2O[106]. Reaction of OPF_3 with H_2O is slow at low temperature, yielding HF and fluorophosphoric acids, viz.

$$OPF_3 + H_2O \rightarrow [HF + HO_2PF_2] \xrightarrow{2H_2O} 3\ HF + H_3PO_4 \qquad (30)$$

Unlike PF_3 and SPF_3, OPF_3 forms an adduct with BF_3[27], but it is

still a very weak acceptor molecule. Lustig and Ruff[90] have recently shown that CsF and OPF_3 form an adduct, viz.

$$2\ CsF + 2\ OPF_3 \rightarrow CsPF_2O_2 + CsPF_6 \qquad (31)$$

illustrating further acceptor properties of OPF_3.

In conjunction with OPF_3, a second P-O-F derivative of considerable commercial importance as an intermediate to the flurophosphoric acid salts found in toothpastes, fertilizer, etc. is μ-oxo-difluorophosphoryl ($P_2O_3F_4$, often referred to as difluorophosphoric acid anhydride).

Preparation. This compound has previously been synthesized by initiating the reaction of PF_3 and O_2 with a silent electrical discharge [171]. Robinson[134] has shown that $(F_2PO)_2O$ can be prepared by the dehydration of $(F_2PO)OH$ with P_4O_{10} and Roesky[136] has extended this approach by using $ClSO_2NCO$ as a dehydrating agent. Recently an elegant but sometimes explosive method of synthesizing $(F_2PO)_2O$ has been reported[20] which consists of photolysis of OPF_2Br with excess O_2 using an immersion lamp with a 2.5 watt output at 2537 Å. Muenow, Uy, and Margrave[114] have observed $(F_2PO)_2O$ as well as OPF_3 and many high molecular weight phosphorus oxyfluoride polymers when fluorinated samples of reagent grade P_4O_{10} were vaporized into a mass spectrometer at 25°-35°.

Reactions: The most common reaction one observes with $(F_2PO)_2O$ is its instantaneous hydrolysis to form the difluoro acid $(F_2PO)OH$[20], even with vacuum lines dried previously by various drying agents. Roesky[136,135] has shown that if $(F_2PO)_2O$ is attacked by a nucleophilic agent (L^-, e.g. Cl^- or SCN^-), cleavage occurs in the phosphorus-oxygen bridge forming $(F_2PO)L$ and $(F_2PO)O^-$. Likewise, attack by a neutral species[137] (e.g. H_2O, PCl_5, NH_3) with moderately easy displaced groups

yields a replacement reaction with P-O-P bridge bond cleavage on $(F_2PO)_2O$, viz.

$$(F_2PO)_2O + PCl_5 \rightarrow 2\ ClF_2PO + Cl_3PO \qquad (32)$$

For example, Kongprich and Preusse[80] reported that in the reaction of NH_3 and $(F_2PO)_2O$ the P-O bond was again cleaved forming H_2NPOF_2 and $[NH_4][PO_2F_2]$ in contrast to the reaction of NH_3 and $(Cl_2PO)_2O$[37] where NH_4Cl and $[(H_2N)_2PO]_2O$ are formed. This indicates the relative decrease in bond strength from (P-F), (P-O) to (P-Cl).

D. Thiophosphoryl Fluoride.

Preparation. The standard fluorinating agents were first used in the methathetical reactions on $SPCl_3$. For example, in 1888 Thorpe and Rodger[162] first synthesized SPF_3, viz.

$$SPCl_3 + AsF_3 \xrightarrow{150°} SPF_3 + AsCl_3 \qquad (33)$$

in a sealed glass tube. BiF_3 and PbF_2 were also employed in this fluorination. Thiophosphoryl fluoride was later prepared by the analogous OPF_3 synthesis, that of heating mixtures of P_4S_{10} and PbF_2[181] or BiF_3[181].

An exchange reaction has also been employed[129]

$$PF_3Cl_2 + S \rightarrow SPF_3 + Cl_2 \qquad (34)$$

where PF_3Cl_2 can be prepared by the direct reaction of PF_3 and Cl_2 (see Reactions of PF_3).

SbF_3 has been successfully employed as a fluorinating agent for $SPCl_3$[26,23,123] and $SPBr_3$[25] with the best results being obtained at atmospheric pressure or greater.

As with OPF_3, NaF[165] in a high dielectric constant medium, and potassium fluorosulfinate[141] have also been used as fluorinating agents.

More recently, Hagen and MacDiarmid[61] have reported the synthesis of SPF_3 by the reaction of P_4S_{10} and PF_3 at 4000 atmospheres and 300° in Au tubing.

Chemical Properties of SPF_3. In the original preparation of SPF_3, Thorpe and Rodger[162] reported that the compound was flammable in air and decomposed when heated above 300° yielding S and PF_3, viz.

$$SPF_3 \xrightarrow{300°} S + PF_3 \qquad (35)$$

SPF_3 reacts readily with Cr or Mn metal at 250°, viz.[170]

$$Cr \text{ or } Mn + SPF_3 \rightarrow Cr_2S_3 \text{ or } MnS + PF_3 \qquad (36)$$

The rate of hydrolysis of SPF_3 is slow as is that of OPF_3, yielding H_2S, HF and H_3PO_4.

It has been shown[25] that SPF_3 does not adduct with BF_3 as does OPF_3. Thorpe and Rodgers[162] did report that SPF_3 and NH_3 react to give $SPF(NH_2)_2$ in their original synthetic paper.

Cavell[25] observed a series of products in the reaction of SPF_3 and Me_2NH, one of which was the monosubstituted $SPF_2(NMe_2)$ plus complex salts.

Lustig and Ruff[90] have reported that KF reacts with $SPCl_3$, viz.

$$8\ KF + 2\ SPCl_3 \rightarrow KPF_2S_2 + KPF_6 + 8\ KCl \qquad (37)$$

which is an analogous reaction found with OPF_3 with the exclusion of the metathetical fluorination.

E. Selenophosphoryl Fluoride.

Preparation. $SePF_3$ was first reported in 1969 by Chaigneau and

Santarromana[31] as a by-product of the reduction of the Group VIA non-metal oxides by PF_3, viz.

$$SeO_2 + 2\ PF_3 \rightarrow Se + 2\ OPF_3 \qquad (38)$$

The reaction was observed at 400° in a system where PF_3 was continuously flowing over the SeO_2. A mass spectral analysis of the volatile products indicated the presence of $SePF_3$, which was attributed to the secondary reaction, viz.

$$Se + PF_3 \rightarrow SePF_3 \qquad (39)$$

Although $SePCl_3$[17] has been prepared and characterized, no previous report or characterization of $SePF_3$ is available.

No physical or chemical data is available on $SePF_3$, but one might expect this compound to be photosensitive because of the photoelectronic and photoconductive properties of Se[39].

F. Tellurophosphoryl Fluoride.

There are no reports of this compound ever having been isolated. Chaigneau and Santarromana[31] have reacted TeO_2 and PF_3 at 450° in the flow system previously described. The only product isolated was OPF_3 resulting from the reduction of TeO_2.

G. Transition Metal Complexes with Phosphorus Trifluoride.

Preparation. In 1886, Moissan[105,99] prepared the first coordination compound containing a fluorophosphine ligand by passing PF_5 over platinum sponge at dull red heat, this volatile substance had the empirical formula $PtPF_5$ which corresponds to $PtF_2 \cdot PF_3$. Not until 1950 was PF_3 coordination chemistry investigated further when Chatt[34,35]

passed PF_3 over $PtCl_2$ at 200° producing the authentic complex $PtCl_2 \cdot 2PF_3$ which dimerizes at a higher temperature to form $[PtCl_2 \cdot PF_3]_2$.

$Ni(PF_3)_4$ has been prepared by several metathetical reactions of $Ni(PCl_3)_4$ and fluorinating agents such as SbF_3[176]. The exchange reaction of $Ni(PCl_3)_4$ and PF_3 yields $Ni(PF_3)_4$[180]. Several attempts have been made to exchange PF_3 for CO in $Ni(CO)_4$[35] but only recently[21] has this been accomplished. Total PF_3 substitution of CO is difficult at best in the metal carbonyls.

Hair and Robinson[62] have reported the formation of 2 $RuO_4 \cdot PF_3$ and 2 $OsO_4 \cdot PF_3$ from the reaction of the tetroxides and PF_3. They have also reported the reaction of PF_3 with some transition metal fluorides to give products such as $F_3P \cdot OsF_2$, $F_3P \cdot IrF_2$, $F_3P \cdot PdF_2$ and $F_3P \cdot CoF$.

Complexes of Group VI transition metals such as Cr and Mo have been obtained by a number of methods[82], viz.

$$M(C_6H_6)_2 + 6\ PF_3 \rightarrow M(PF_3)_6 + 2\ C_6H_6 \quad (M = Cr, Mo, W) \qquad (40)$$

$$Cr(NH_3)_3(CO)_3 + 3\ PF_3 \rightarrow Cr(PF_3)_3(CO)_3 + 3\ NH_3 \qquad (41)$$

$$[C_6H_3(CH_3)_3]Mo(CO)_3 + 3\ PF_3 \rightarrow Mo(PF_3)_3(CO)_3 + C_6H_3(CH_3)_3 \qquad (42)$$

Nickel, palladium and platinum[83] have been found to react directly with PF_3 to form the corresponding tetracoordinate complexes, viz.

$$M + 4\ PF_3 \rightarrow M(PF_3)_4 \quad [M = Ni, Pd, Pt] \qquad (43)$$

The most important method of synthesis, particularly with respect to simplicity of the starting materials, applicability to a wide range of metals, and high yields, is the "reductive fluorophosphination" of metal salts[70].

In this synthetic procedure an anhydrous metal halide is reduced

in an autoclave by a halogen accepting metal (generally Cu or Zn) with addition of PF_3 to the metal liberated under high PF_3 pressure (300 - 400 atmospheres) and temperature in the 100°-300° range.

$$MX_m \xrightarrow[>RT]{PF_3,\ Cu} \begin{cases} \longrightarrow M(PF_3)_n + mCuX \\ \longrightarrow xM(PF_3)_n + (m-1)\ CuX \\ \xrightarrow{1/2\ H_2} H_yM(PF_3)_n + mCuX \quad (y = 1,2) \end{cases} \tag{44}$$

Timms[159] has recently described very interesting syntheses of several metal-trifluorophosphine complexes using the technique of co-condensing vapors of transition metals (formed at temperatures between 1300° and 1700°) with PF_3 at liquid nitrogen temperature. Chromium, nickel, cobalt, and iron readily afford the known PF_3 complexes.

Chemical Properties. This class of compounds is distinctively similar to the corresponding transition metal carbonyls[71]. They are remarkably stable towards oxidizing agents and moisture. Many can even be steam distilled. These high molecular weight compounds are distinguished in particular by their high volatility which probably results from a strong mutual repulsion due to the high electron density on the ligands.

Dilute or concentrated acids attack the metal trifluorophosphines only when hot; bases, on the other hand, rapidly hydrolyze the P-F bonds.

Ammonolysis of $Ni(PF_3)_4$[140] in liquid NH_3 leads initially to a colorless solution, viz.

$$Ni(PF_3)_4 + 24\ NH_3 \rightarrow Ni[P(NH_2)_3]_4 + 12\ NH_4F \tag{45}$$

Upon concentration, the complex undergoes polycondensation with liberation of NH_3 to form a viscous mass which is evidently the highly

polymeric nitride $[Ni(PN)_4]_x$. Similar condensations have been observed with primary amines[140].

Silicon-Cobalt-Carbonyl-Phosphorus Trifluoride Compounds. Kettle[78] first synthesized a silicon cobalt tetracarbonyl by the reaction of tetravinyl silane with $Co_2(CO)_8$ in refluxing petroleum ether. The material had the postulated composition $H_2C{=}CHSi[Co(CO_3)]_3$ and was believed to have the general formula $RC[Co(CO)_3]_3$. Several compounds of the type $R_3SiCo(CO)_4$[32] (where R=H, Cl, H_3Co, C_2H_5) were reported in 1965.

Due to the acidity of a silicon hydrogen as compared to the carbon hydrogen, Si-Co bonds can be formed by direct reaction of silanes with $Co_2(CO)_8$, viz.

$$SiX_yH_{(4-y)} + Co_2(CO)_8 \rightarrow SiX_yH_{(3-y)}Co(CO)_4 \qquad (46)$$

where X = halogen or R (organic group).

These reactions[78], can usually be carried out at an autogenous pressure of the silane at room temperature. The synthesis of $Cl_3SiCo(CO)_4$ can be carried out in this manner[32],

$$Co_2(CO)_8 + 2\ Cl_3SiH \rightarrow 2\ Cl_3SiCo(CO)_4 + H_2 \qquad (47)$$

Another method that may be used in the preparation of silicon cobalt tetracarbonyls is that of reaction of a silane with $H\text{-}Co(CO)_4$, cleaving the H-Co bonds[14].

Of particular interest in this investigation will be the chemistry of polynuclear silicon-cobalt carbonyls and phosphorus trifluoride systems. Two research groups have shown extensive interest in metal carbonyl-phosphorus trifluoride systems in general, that of Kruck and

R. Clark. As a silicon chemist Professor A. G. MacDiarmid[92] has also exhibited an interest in silicon-metal-carbonyl-phosphorus trifluoride systems.

Warren, Busch and Clark[172] have shown that the substitution of PF_3 for CO is facile, resulting in all substitution compositions for a large series of metal carbonyl compounds. The substitution of PF_3 for CO appears to be a near random process. Nixon[120] has recently reviewed the various aspects of fluorophosphine chemistry, emphasizing NMR studies which indicate that electronically a given ligand seems basically indifferent to the relative distribution of CO and PF_3 that surround it. Due to great similarity in CO and PF_3, the biggest effect caused by substitution of PF_3 for CO is that of the difference in the symmetry of CO and PF_3.

There are some changes in the formation of polynuclear complexes with PF_3, probably due to the inability of PF_3 to bridge bond as CO is known to do. For example, Clark[36] has shown that although ultraviolet irradiation of $Fe(CO)_5$ produces $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$, if at least one PF_3 group is present in the starting material ($Fe(CO)_4PF_3$), no diiron or triiron compounds are found after extensive irradiation. After many hours of irradiation, trace amounts of $[(PF_3)_3Fe(PF_2)]_2$ are produced[166].

Extensive PF_3 substitution on $Ru_3(CO)_{12}$ yields the monomer up to the totally substituted $Ru(PF_3)_5$[167].

Kruck and Lang[85] have reported the formation of the cobalt-PF_3 bridge compound $[(PF_3)_3Co(PF_2)]_2$. The complex was formed by the reaction of CoI_2 and PF_3, viz.

$$CoI_2 + PF_3 \rightarrow (PF_3)_3Co(PF_2)_2Co(PF_3)_3 + \text{other species } 30\% \qquad (48)$$

The structure of the species is postulated from infrared, N.M.R., elemental analysis, and mass spectral data. The F-19 N.M.R. consisted of two doublets, one with J_{PF}=1330 Hz for terminal PF_3 and another with J_{PF}=1230 Hz for the PF_2 bridges. The chemical shifts were +792 Hz and +2820 Hz respectively, relative to $CFCl_3$.

Dimetallic hexacarbonyl acetylenes have recently been described by Seyforth and White[145]. Silicon, germanium and tin substituted acetylenes were mixed with equimolar quantities of $Co_2(CO)_8$ in dry hexane under an argon atmosphere. The mixture was stirred overnight at room temperature and filtered at -78°. The structure of these complexes is believed to basically have a tetrahedral core with the two acetylene carbons and the two cobalts at the corners of the tetrahedron.

MacDiarmid has recently reported in a private communication[92] that $Cl_3SiCo(CO)_4$ reacts with PF_3 at 100° to yield 95% monosubstitution and 5% disubstitution of PF_3 for CO. The reaction was attempted thermally at 100° under autogenous pressure. The F-19 N.M.R. consisted of two doublets, one with J_{PF}=1361 Hz (monosubstitution) and a second with J_{PF}=1325 Hz (disubstitution). The chemical shifts were +1059 Hz and +1032 Hz respectively relative to $CFCl_3$, for a 0.75 molar solution in CH_2Cl_2.

H. Organic Fluorochlorocarbons.

Organic fluorochlorocarbons fall into two general classes, those containing one carbon and those containing two or more carbons. Both

classes of compounds are extremely stable and non-reactive with the "Freon" gases[64] and polymeric "Teflon"[64] being representative of the chemical non-reactivity.

Hamilton[64] provides an extensive review on the synthesis of the lower carbon content fluorochlorocarbons in industry. Barbour, Belf and Buxton[16] provide an excellent review of the synthesis of the fluorochlorocarbons by halogen exchange with emphasis on the more exotic derivatives.

This discussion will deal with the synthesis of single carbon fluorochlorocarbons. The $CCl_xF_{(4-x)}$ class of fluorochlorocarbon is most conveniently prepared by the fluorination of a lower fluorine content species with fluorine replacing chlorine. The reason for chlorine displacement by fluorine is discussed by Parker[125]. This argument is simply that the C-F bond energy is much greater than the C-Cl bond energy and thus more difficult to break and more thermodynamically favored to form. As an example, the relative bond dissociation energies of methyl fluoride and methyl chloride are +107 and 81 Kcal/mole respectively[51].

Many different fluorinating agents have been used. It has been observed that gaseous HF will react slowly with CCl_4, viz.[92]

$$(4-x)HF + CCl_4 \rightarrow (4-x)HCl + CCl_xF_{(4-x)}. \qquad (49)$$

High pressures and elevated temperature are required for practical industrial rates of production. The present methods of synthesis of fluorochloromethanes involves the use of numerous catalysts in the fluorination process. The best example is that of using HF and $SbCl_xF_{(5-x)}$, viz.[64]

$$CCl_4 + (y-4)\ HF \xrightarrow{SbCl_xF_{(5-x)}} CCl_yF_{(y-4)} + (y-4)HCl \qquad (50)$$

The yield of various fluorochloromethanes can be controlled by varying the specific catalyst used along with the reaction conditions.

Chemical Properties of the Fluorochlorocarbons. The reactions of the fluorocarbons are quite limited. As indicated in the synthetic section, reactions involving the displacement of chlorine by fluorine are quite common and have been studied extensively for commercial reasons[83].

Wittstruck et. al.[179] have shown that some fluorocarbons form hydrates. Two examples are $CCl_3F \cdot 16.6\ H_2O$ and $CCl_2F_2 \cdot 15.6\ H_2O$ with decomposition temperatures of 8.5° and 12.1° respectively. This property of these fluorocarbons has been used by various researchers in the desalination of seawater[157].

In 1961, Eiseman[45] reported that the very stable "Freons" react violently when molten Al is dropped in the liquid fluorocarbon. The Al(l) burns at white heat in a self sustaining reaction when dropped into CF_2Cl_2(l). With $CFCl_3$(l) the Al(l) will stop burning a few seconds after being dropped into the liquid fluorocarbon. The products in the reaction were $AlCl_3$(s), AlF_3(s) and C(s).

Homann and MacLeon[75] have reported that CF_2Cl_2 and $CFCl_3$ burn with F_2 at 1 atmosphere to yield higher fluorinated single carbons. With the limited addition of H_2 to the flame a partially hydrogenated fluorocarbon is formed along with fully halogenated two carbon products. Increasing the amount of H_2 in the mixture finally leads to only HCl, HF and C as products of the combustion. The addition of H_2 to the

combustion mixture increased the flame temperature proportionately.

In 1962 it was reported[43] in the form of a patent that the use of chlorofluoroalkanes, particularly $CFCl_3$, in an aerosol can when the fluid to be sprayed contains a primary or secondary alcohol is hazardous because of the possible formation of aldehydes or ketones along with halogenated acids (usually HCl). The patent states that the addition of a mononitroalkane such as nitromethane, nitroethane, 2-nitropropane or 1-nitropropane to 5% of the total weight inhibits the reaction up to 6 months. Robey[133] recently reported that a mixture of ethanol and $CFCl_3$ was stable when heated to 75° for 24 hours in a pressure vessel (100 atmospheres).

Steudel[153] has recently studied the pyrolysis of several halocarbons. In the pyrolysis of CCl_4 (900°) Cl_2, CCl_3, C_2Cl_6, C_2Cl_4, and C were determined as decomposition products. In the pyrolysis of $CFCl_3$ (with Ag at 700°) trans - $C_2F_2Cl_2$ was identified along with other products. At these temperatures, mechanisms are proposed on the basis of the initial formation of CCl_3 (identified by matrix isolation infrared spectroscopy) and subsequent reactions of the $\cdot CCl_3$ and $Cl\cdot$.

Another paper by Steudel[157] reports the reduced pressure (0.2 torr) elevated temperature (450° - 600°) reaction of CCl_4 with Te, Ag and Br to yield C_2Cl_6, MCl and CCl_3Br. A matrix isolation (CCl_4) spectral study of the recombination of CCl_3 to form C_2Cl_6 indicates that the reaction is first order.

Fells and Moelwyn-Hughes[50] and Hill[72] have studied the hydrolysis of CCl_4 by H_2O in the condensed phase below 100°. They have established

that the hydrolysis produces CO_2 and HCl and is first order with respect to CCl_4. These authors consider that the decomposition of CCl_4 is the rate determining reaction step with the formation of the intermediate CCl_3OH which rapidly decomposes to HCl and CO_2.

Takao[65] has studied the hydrolysis of CF_2ClH in a basic solution near room temperature. He proposed a mechanism where the base would extract the acidic hydrogen leaving CF_2Cl^- which would decompose rapidly to $:CF_2$ and Cl^- with subsequent basic hydrolysis. The high susceptability to hydrolysis of $CHClF_2$ was attributed to the easily ionizable hydrogen atom in the molecule, but no discussion was given to the order of the reaction.

Recently Gaisinovich and Ketov[52] have studied the high temperature hydrolysis of carbon tetrachloride and phosgene in the gas phase. They observed that appreciable hydrolysis of CCl_4 begins above 300° (at 350° there is approximately 5% hydrolysis per hour). It was also noted that Cl_2Co was observed in the gas phase hydrolysis of CCl_4 whereas this product had not been reported in the liquid (100°) CCl_4 hydrolysis[50,72]. The degree of hydrolysis of CCl_4 and Cl_2CO was plotted against time for several temperatures. Analysis of the plots shows the reactions to be second order with respect to CCl_4 and Cl_2CO. The plot the log of the concentration of CCl_4 versus 1/T shows two linear sections, with the point of inflection at 450°. The explanation given is that CCl_4 decomposes at this temperature giving C_2Cl_6 and Cl_2, with the rate of hydrolysis of C_2Cl_6 being slower than CCl_4. This slower rate of hydrolysis accounts for the inflection in the plot. In general, the gas phase hydrolysis is mechanically different than the low temperature

liquid phase hydrolysis since it is second order and the intermediate Cl_2CO is momentarily observed in the gas phase. The hydrolysis is then considered to be a two step process,

Step 1 $$CCl_4 + H_2O \rightarrow Cl_2CO + 2\ HCl \quad (51)$$

Step 2 $$Cl_2CO + H_2O \rightarrow CO_2 + 2\ HCl \quad (52)$$

CHAPTER II

EXPERIMENTAL

A. Vacuum System and Techniques.

The basic principles of vacuum line technique have been described elsewhere[77]. Therefore, only the aspects pertaining to this work are summarized below.

1. Vacuum System: The vacuum system was constructed of borosilicate (Pyrex 7740) glass and equipped with precision ground glass or Teflon (Fischer and Porter #795-005-0004) stopcocks. The standard taper 12/30 removable joints were lubricated with Halocarbon grease and the stopcocks were lubricated with Apiezon M grease. The system was evacuated using a Model 1400 "Welch Duo-Seal" fore-pump in series with a liquid nitrogen trap. The vacuum system was evacuated to 10^{-3} to 10^{-4} torr (1 torr = 1 mm Hg) before handling a material.

2. Pressure Measurements: Pressure measurements, below atmospheric pressure, were made using a mercury manometer. The pressure was read with a meter stick calibrated in millimeters and could be read to approximately ± 0.3 mm.

3. Temperature Measurements: Low temperature measurements were made using a pentane in glass thermometer (accurate to ± 2°). When higher accuracy was desired an iron-constantan thermocouple was

used. A Leeds and Northup potentiometer (Model 8690) with a fixed junction at 0° was used with the thermocouple.

Room temperature measurements for molecular weight determinations were made with a thermometer which could be read to ± 0.3° suspended from the vacuum system.

Temperatures above room temperature were measured with a mercury in glass thermometer to ± 0.5° or with an iron-constantan thermometer to ± 0.5°.

4. Production of Low Temperatures: Liquid nitrogen in Dewar flasks was used to maintain temperatures at -196°. Temperatures below ambient were maintained by the use of "slush" baths made by partially freezing appropriate solvents (Table II) and then allowing the frozen material to melt.

Temperatures near the sublimation point of CO_2 (-78°) were obtained as either acetone or isopropanol mixtures of "dry ice" and the solvent.

5. Separation of Volatile Materials: Mixtures of volatile materials were separated by fractional condensation in, or distillations from, traps maintained at low temperatures. The notation that will be used to facilitate descriptions of the various separations are as follows:

$$RT \sim \underset{A}{-96^\circ} \sim -196^\circ \quad \text{(n times)}$$

$$(-23^\circ \text{ and } RT) \sim \underset{(B)}{-134^\circ} \sim \underset{(C)}{-196^\circ} \text{ (n times)}$$

This means that a mixture was allowed to warm to room temperature (RT) from -196° without applying any external heat, without pumping, and as soon as all of the material had distilled the stopcocks on the traps were closed. In special circumstances distillations were carried out

TABLE II

Liquids Suitable for Constant Low Temperature Baths[a]

Compound	Approximate Freezing Point °C
Benzene	+ 5.5
Water	0.0
Aniline	- 6.6
Carbon tetrachloride	- 22.9
Bromobenzene	- 30.9
Chlorobenzene	- 45.2
Chloroform	- 63.5
Carbon dioxide[b]	- 78.0
Toluene	- 95.0
Carbon disulphide	-111.6
Methylcyclohexane	-126.3
n-Pentane	-131.5
iso-Pentane	-160.5

[a]A "slush" bath in which solid-liquid equilibrium is maintained.

[b]The -78° bath is dry ice with acetone or isopropanol as conductive solvent. A fresh bath may reach -81°.

with pumping. In such instances, this is specifically stated. The symbol "∿" signifies that the material was distilling from a trap at one temperature to a trap of another temperature. In the above illustration, the material was passed through traps held at -96° and then condensed in a trap held at -196°. A vertical arrow indicates that a new distillation scheme was employed. In the above scheme, (-23° and RT) means that the trap was surrounded by a -23° bath for a certain period of time and was then warmed to room temperature. A capital letter Signifies a fraction which las later examined. If no capital letter is present under a trap, this signifies that either the fraction in that trap was not examined or that there was no material in the trap. The "n times" signifies the following operations upon the underlined trap:

RT ∿ -96° ∿ -196° (n=1)

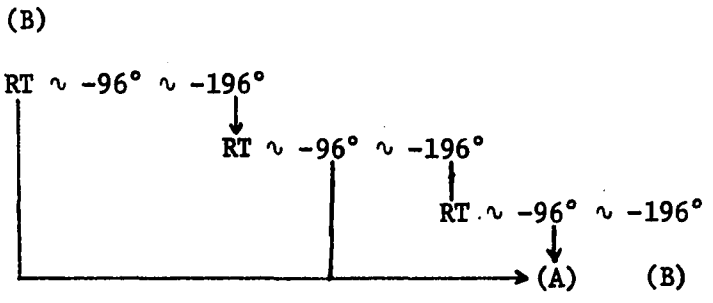
↓

RT ∿ -96° ∿ -196° (n=2)

↓

RT ∿ $\underline{\text{-96°}}_{\text{(A)}}$ ∿ $\underline{\text{-196°}}_{\text{(B)}}$ (n=3)

The process ends when n is reached, that is, when no more material is observed in the -196° trap. The process was then continued until no additional material is found in the -196° trap.



Fractions with the same capital letter are combined.

6. Molecular Weight Measurement: The molecular weight (MW) of volatile compounds was carried out using the method of Dumas. In such determinations the gas was assumed to follow the ideal gas equation as the pressure did not exceed 0.5 atmospheres. Therefore, the weight of the gas at a known temperature, pressure, and volume permitted the calculation of the molecular weight from the equation of state for an ideal gas,

$$PV = nRT = \frac{g}{MW} RT$$

thus,

$$MW = gRT/PV$$

Where P = Pressure in atmospheres
V = volume in liters
R = Gas constant 0.08205 ℓ atmos/°K mole
g = Weight of sample in grams
T = Temperature, °K
MW = Molecular weight

Molecular weights of a two component mixture ("mixed molecular weight") was determined by use of the equation:

$$M = f_1 MW_1 + f_2 MW_2$$

where f_1, f_2 = Mole fraction of component

MW_1, MW_2 = Molecular weight of 1 and 2

M = Average molecular weight.

Care was taken not to carry out molecular weight determinations at the saturation vapor pressure at room temperature of the materials under study. In such circumstances the molecular weight could be made erroneous due to adsorption on the glass surfaces of the molecular weight bulb.

7. Criteria of Purity: The purity of materials used in this research was checked by at least two of the following procedures:

a. Molecular weight so that the error in the difference between the calculated and experimental valve did not exceed 1% of the calculated value.

b. Vapor Pressure at a known temperature to within 1% of the calculated (or literature) value or to within approximately ± 2.0 torr, whichever was the least.

c. Infrared spectrum to agree with a published spectrum or to a spectrum previously determined in this laboratory on the pure material.

d. Mass spectral fragmentation pattern. The mass spectra of mixed or pure compounds were frequently recorded in order to determine whether the fragmentation pattern was consistent with that of the mixture or pure compound from literature values or standard "blank" spectra. When feasible, the identification of the parent molecular ion when studying a pure compound was considered to be of considerable importance. If fragments of higher mass number than that of the molecular ion of a presumably pure compound were obtained then the presence of high molecular weight impurities could be assumed.

Due to the high sensitivity of the mass spectrometer, it was used extensively for qualitative and gross quantitative interpretations of purity for reactants and products.

e. Nuclear magnetic resonance spectrum: agreement with the expected ratio of the area under the resonance signals, the position of chemical shifts and the nature of the fine structure observed in the signals. In addition, the absence of extraneous signals indicates the purity of a compound.

f. Melting point determinations to ± 0.5° of the literature value and a range not exceeding 1.5°.

B. Pressure Equipment and Techniques.

The use of pressure equipment as a routine tool for synthesis has not been extensive, therefore the apparatus and new techniques used in this research will be described in detail.

1. General Description of High Pressure Apparatus: The high pressure system was modeled after one designed by Dr. J. J. Moscony and Professor A. G. MacDiarmid[112] specifically to be used in conjunction with a high vacuum system. The intensifier and microreactors were purchased from HIP - Autoclave Engineers, Erie, Pennsylvania. The details on the model system have been published by Moscony, Harker and MacDiarmid[113]. A diagram of the model system is shown in Appendix A. The plumbing in the system allows for the use of one or more microreactors simultaneously with the simple addition of Tee fittings.

The presence of very high pressures compels the experimenter to exercise extreme caution at all times. The intensifier used in this research was enclosed in one quarter inch steel plate. The microreactors were rated at 4000 atmospheres and 600° and the plumbing had a similar room temperature rating. Safety goggles, leather gloves and a leather jacket were available to the experimenter.

In the original apparatus one of the reactants was loaded directly into the microreactor and the other reactant (gaseous) was used as a pressuring medium. This option was also available on the apparatus used in this work but was not used because of the high cost of the reactant gas and its reactivity with metals at high pressure and elevated

temperature. This research was carried out using the technique of encapsulating the reactants in a non-reactive, malleable material. Using this technique, the pressuring medium could be gas or liquid with the pressure being transferred to the reactants through the malleable capsule wall.

The procedure used in this research was developed by Hagen[60] using gold tubing as the encapsulating material and nitrogen gas as a pressuring medium.

Using this procedure the reactants were sealed in vacuo in gold tubes at -196°. The gold tube was then transferred to a microreactor cooled to -196° and pressured to 3000 atmospheres. The microreactor was then heated to the desired temperature and pressure (excess pressure was bled off).

For example, in section G-2, a mixture of PF_3 and O_2 was sealed in a gold tube and pressured at 4000 atmospheres and 300° for 12 hours. The tube was then opened to the vacuum system and the volatiles (86% based on initial PF_3) recovered.

The operations involved in preparing a sample in a gold tube will be demonstrated by an example. Consider the reaction of PF_3 and O_2 mentioned above.

(1) A length of gold tubing (3.0 mm o.d., 2.9 mm i.d., 25. cm long) was flattened for 1 cm at one end with a pair of pliers having tape on the jaws so the gold would not be creased. The flattened end of the tube was then heated in a CH_4/O_2 glass blowers torch, melting the gold and sealing the end of the tube.

(2) The open end of the gold tube was then inserted into the lower

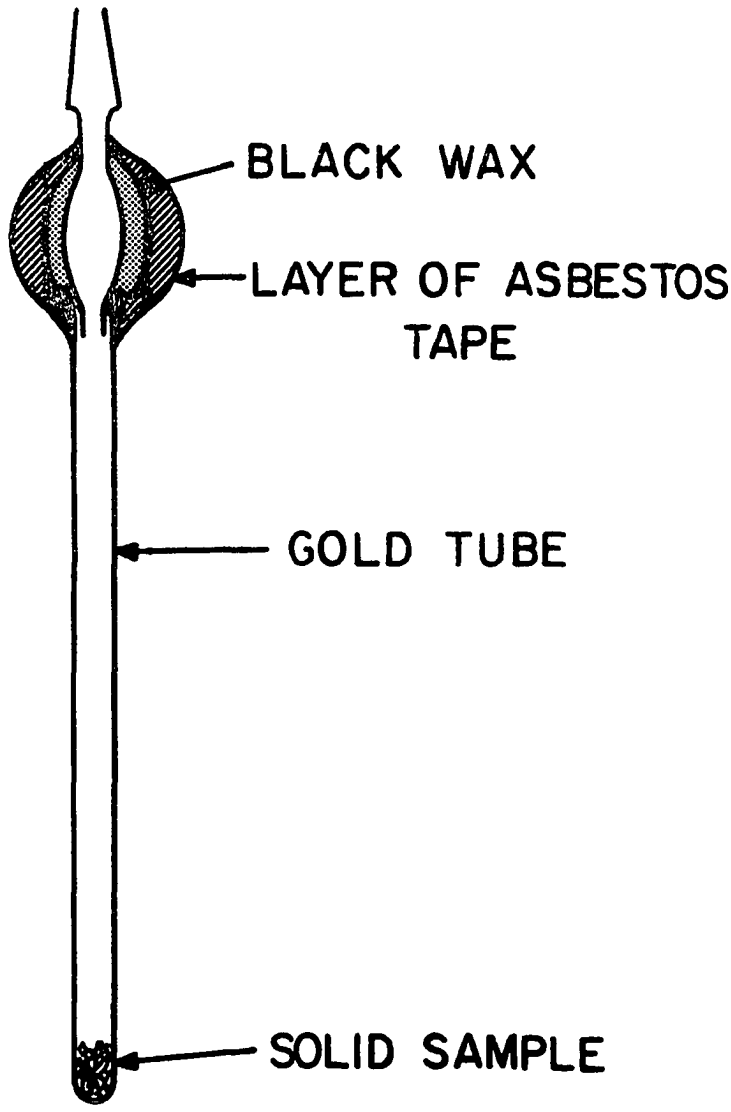


Figure 1. Gold Tube Prepared for Sealing

end of a ℔ 12/30 male joint (Figure 1). The glass-gold junction was then heated lightly in an open flame. After removal from the flame, "black wax" (picein wax) was applied to the hot junction which upon cooling formed a vacuum tight seal.

(3) At this time solid reactants could be added to the gold tube with the amount added being determined by weight differences from a weighing bottle. If necessary, the addition could be carried out in a nitrogen bag or suitable inert atmosphere.

(4) The assembly was then evacuated and allowed to stand open only to the manometer for one hour. If no pressure was observed on the manometer the tube was declared leak free. At this point, a length of asbestos tape was moistened and wrapped around the seal to insure that the black wax didn't melt while sealing the gold tube (step 7).

(5) The volatile material was then condensed into the gold tube at -196°. The amount of material condensed into the tube was determined using the ideal gas law where the volume (V) was a calibrated volume on the vacuum line, the pressure (P) was the pressure read on the manometer and the temperature (T) was the room temperature measured with a thermometer hanging from the vacuum line. Amounts of reactants having no vapor pressure at -196° were determined by subtracting $n_o = 0.0$ (where P_o is zero at -196°) from some n_1 (where P_1 is the pressure of the calibrated volume). For reactants having some vapor pressure at 0196° (such as O_2) the amount of reactant gas was determined by subtracting the amount of gas left in the calibrated volume n_2 (at some P_2 at -196°) from the amount of gas present initially at atmospheric pressure, n_1 (at atmospheric pressure, P_1).

(6) The tube was then squeezed flat with the padded pliers for 3 cm about 10 cm from the bottom of the tube. Care was taken to crimp the tube flat at the edges near the middle of the sealing area. The flattened portion of the tube was then sealed using a H_2/O_2 hand torch. This operation required a very hot flame about 6 cm in length. The gold tube was heated red hot at the midpoint of the flattened portion to allow the two flat gold surfaces to seal. This was achieved by holding the torch back from the tube. The torch was then brought closer to cut the gold tubing at the top of the seal. The seal was made as close to the liquid nitrogen as possible and the tube was held below the seal with a pair of tweezers. A 99% sealing success can be obtained if done appropriately.

(7) The gold tube was then removed from the -196° Dewar and its length recorded in the research notebook for further identification. The tube was stored in liquid nitrogen until pressurization.

(8) The tube (at -196°) was inserted into the microreactor, which had been corked and cooled to -196°.

(9) The microreactor was then closed and pressurized and the reaction was carried out at a specific pressure and temperature.

(10) After sufficient reaction time, the microreactor was quenched in water, then to -196° before releasing the pressure.

(11) While still at -196°, the microreactor was removed from the pressure system, clamped in a vise, opened, and the gold tube dumped into a -196° bath. The tube was usually flat, except where the solid material was positioned.

(12) The gold tube opener (Figure 2) was connected to the vacuum line

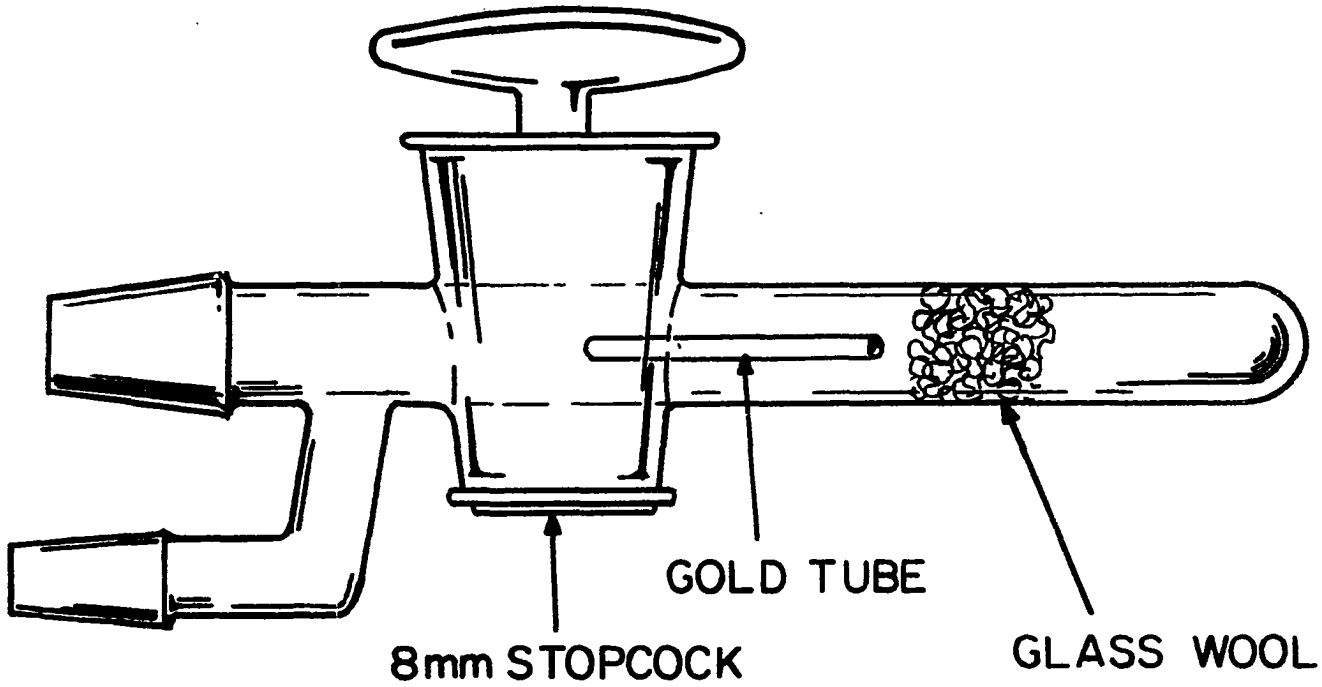


Figure 2. Sealed Tube Opener

through the side arm. Glass beads were positioned in the lower portion of the opener to insure that the top end of the gold tube was positioned within the bore of the large straightbore stopcock.

(13) The glass cap was removed from the top of the opener, the gold tube dropped in and the cap replaced. The opener was then evacuated with intermittant pumping to check for gold tube leaks. If no leak was observed on the manometer, the H_2O was pumped off the outside of the tube through a -196° trap (this H_2O that invariably gets on the cold gold tube when exposed to air is the most limiting feature of this research).

(14) The gold tube was opened by turning the straightbore stopcock through the gold tube, slicing it in two. This can be done with or without liquid nitrogen surrounding it. As the tube is sliced the volatiles are trapped in the first trap at -196° without pumping. Intermittant pumping through the second and third trap at -196° can then be used to remove noncondensibles such as O_2.

(15) At this point the volatile material was identified using standard high vacuum techniques.

C. Glass Pressure Vessels.

It was found that pressure reactions up to 50 atmospheres (ideal gas) could be carried out in a glass pressure reactor[132] similar to that illustrated in Figure 3. The maximum pressure is a function of the wall thickness (Appendix B) and the tensile strength, thus a vessel having an outside diameter of 14 mm and an inside diameter of 8 mm should withstand a pressure of 98 atmospheres.

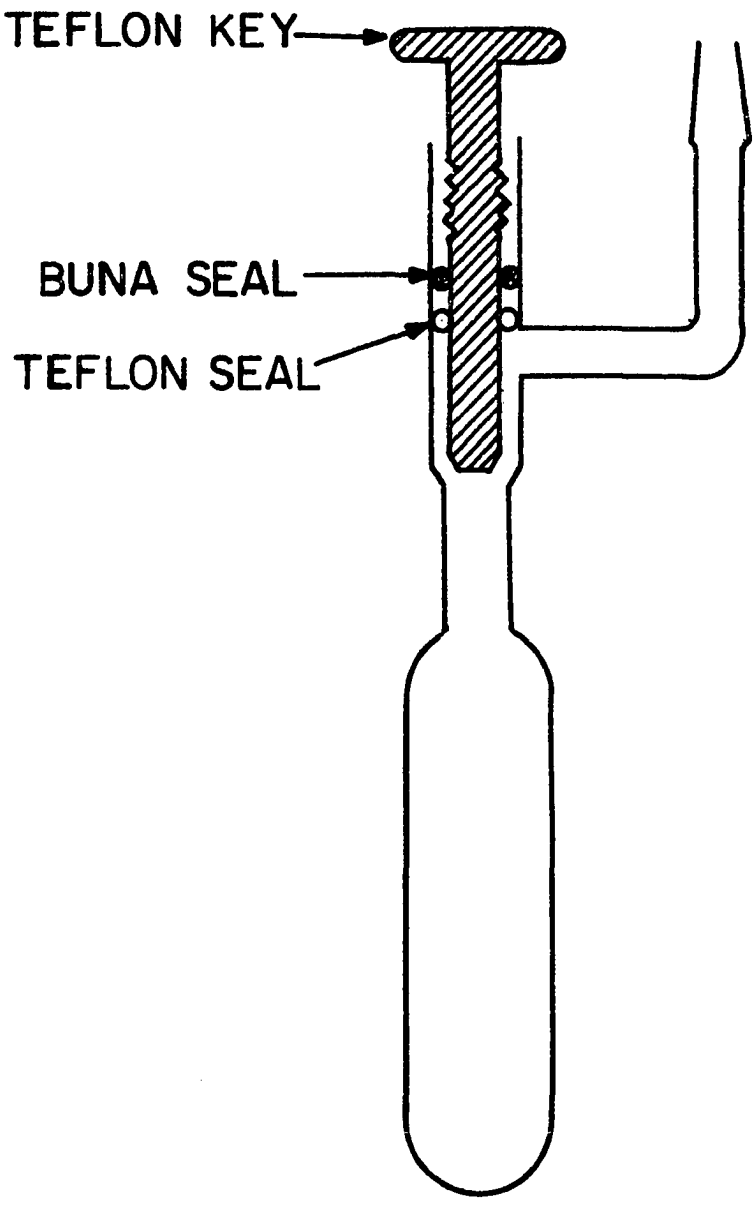


Figure 3. Glass Pressure Reactor

This type of reactor was made from a Fisher and Porter (Warminster, Pa.) 4 mm quick opening angle valve (cat. No. 795-005-004). The autogenous pressure created by a known quantity of gas in a known volume of the pressure vessel at a given temperature was calculated using the ideal gas equation. In using such a vessel at elevated temperatures, the vessel was immersed in the bath up to about 3 cm from the bottom of the Teflon stopcock. The same procedure was applied when cooling the vessel below 0°.

A second glass reactor vessel was designed (Figure 4) to do reactions at or near atmospheric pressure. The maximum pressure rating of the bulb was 10 atmospheres but extensive shielding was used even at the 1 atmosphere maximum pressure of any of the attempted reactions. With a volume of one liter 40 mmoles of reactants could be used at 25° or 20 mmoles of reactants could be used at 300° without exceeding the specified 1 atmosphere pressure limit.

The major advantage of this vessel is that extensive quantities of gaseous reactants can be used at elevated temperature without high pressures. Another advantage is that the coldfinger can be heated to high temperatures (dependent on the glass used) without heating the Teflon Stopcock. Teflon stopcocks have a limited useful temperature range when used for vacuum or pressure seals because they contract when cooled and flow when heated.

D. Spectroscopic Equipment and Techniques.

1. Infrared Absorption Spectra: Infrared absorption spectra were obtained for volatile materials by enclosing a gaseous sample in

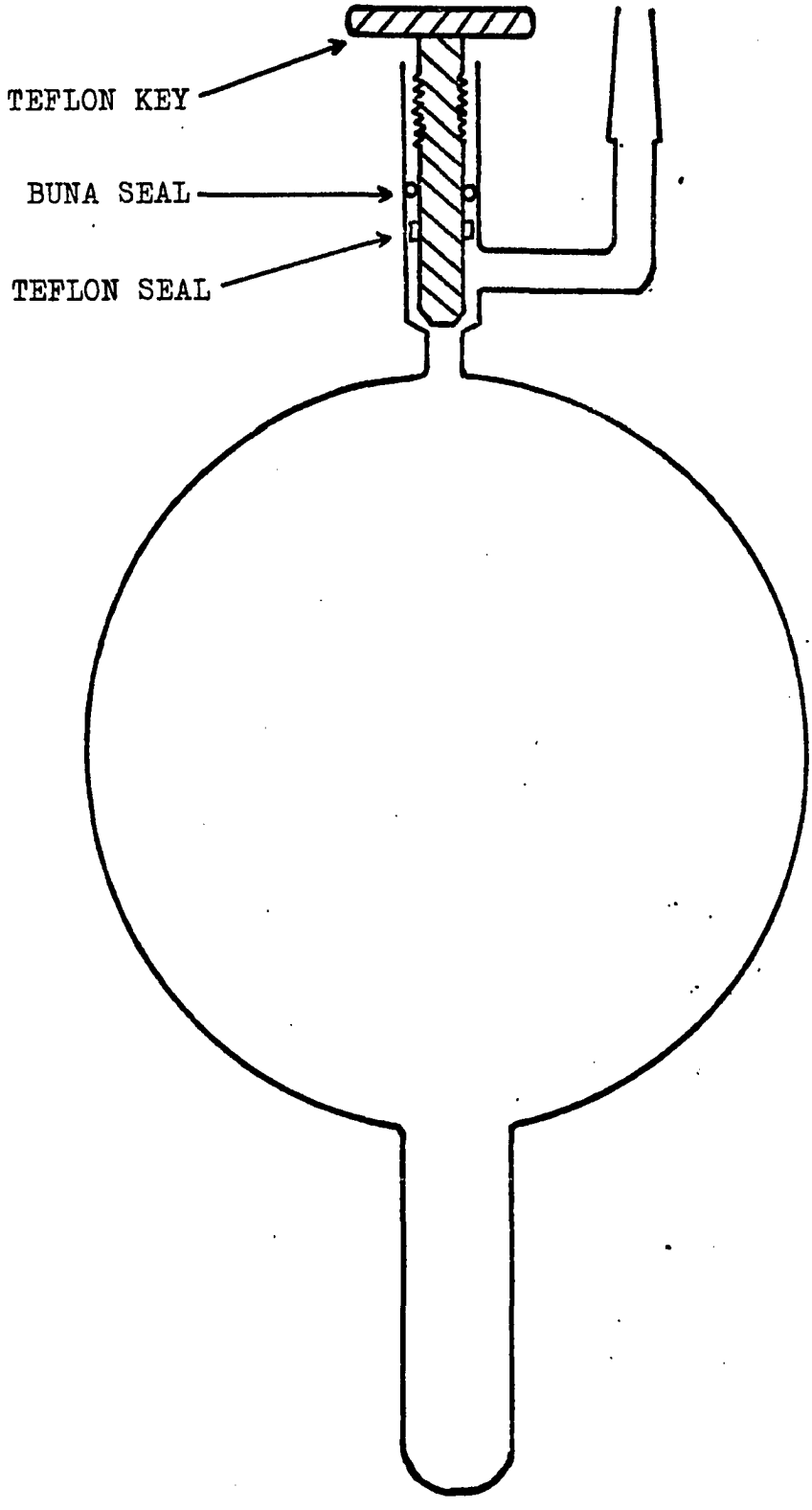


Figure 4. One Liter Reactor

a cell (10 cm path length) fitted with KBr windows (32 mm diameter X 4.0 mm thick) which were sealed with black rubber O-rings. Infrared spectra of solid materials were taken with the solid dispersed in a mull (Nujol mineral oil) or a KBr pellet. When the oils were used the samples were examined as a smear between KBr plates.

Absorption spectra were obtained in the 2.5μ to 40μ region using a Beckman Model IR-10 double beam, grating spectrophotometer. The calibration of the instrument was checked after each spectra with polystyrene film.

2. Mass Spectra: Mass spectral cracking patterns were obtained using a Hitachi-Perkin Elmer RMU-6E Mass Spectrometer. The instrument was operated at an ionization current of 40 microamperes. The ambient operating temperature was 150°, but a low temperature of 40° could be obtained for thermally unstable compounds.

3. Nuclear Magnetic Resonance Spectra: Fluorine-19 nuclear magnetic resonance spectra were obtained from a Varian Associates HA-100X spectrometer operated at a fixed frequency of 95.4 MHz.

Spectra were obtained at an ambient operating temperature of 35° on spinning samples contained in sealed (5 mm o.d.) borosilicate (Pyrex) glass tubes.

Trichlorofluoromethane was used as an internal standard.

E. Reagents.

Carbon Tetrachloride - (CCl_4, Merck, Reagent Grade) was used as obtained. Infrared spectrum[173] and mass spectrum[3] identical to that given in the literature.

Carbon Tetrafluoride - (CF_4, Freon 14, Matheson) was used as obtained after degassing by pumping through a -196° trap. Infrared spectrum[55] and mass spectrum[2] identical to that given in the literature.

Chlorotrifluoromethane - (CF_3Cl, Freon 13, Matheson) was used as obtained after degassing by pumping through a -196° trap. Infrared spectrum[160] and mass spectrum[149] identical to that given in the literature.

Dichlorodifluoromethane - (CF_2Cl_2, Freon 12, Matheson) was used as obtained after degassing by pumping through a -196° trap. Infrared spectrum[118] and mass spectrum[6] identical to that given in the literature.

Fluorotrichloromethane - ($CFCl_3$, Freon 11, Matheson) was used as obtained after degassing by pumping through a -196° trap. Infrared spectrum[69] and mass spectrum[5] identical to that given in the literature.

Magnesium - (Mg, Fisher Scientific) was dried in an oven at 110° for 4 hours and stored in a dessicator when not in use.

Nitrogen - (N_2, Big 3 Industries) was used as obtained as an intensifying medium for the high pressure apparatus. In this research gaseous nitrogen for the glove bag was obtained from a liquid nitrogen cylinder.

Oxygen - (O_2, Big 3 Industries) was used as obtained.

Phosphorus pentafluoride - (PF_5, Matheson) was purified by distillation:

$$RT \sim \underline{-131^\circ} \sim -196^\circ \quad \text{(3 times)}$$
$$\qquad\quad \downarrow \qquad (A)$$
$$RT \sim -96^\circ \sim -196^\circ \quad \text{(3 times)}$$
$$\qquad\quad (B) \qquad (C)$$

Fraction (C) was retained and fractions (A) and (B) were discarded; mol. wgt. calcd. 126.0, found 124.9; the infrared spectrum was identical to the published spectrum.

Phosphorus trifluoride - (PF_3, Ozark-Mahoning Co., Lot. No. KS-7-105) was purified by distillation:

$$RT \sim \underset{A}{-95^\circ} \sim -196^\circ \downarrow$$

$$RT \sim \underset{B}{-131^\circ} \sim \underset{C}{-196^\circ}$$

Fractions (A) and (C) were discarded and fraction (B) retained: mol. wgt. calcd. 87.9, found 87.8; infrared spectrum identical to that given in the literature.

Phosphorylfluoride - OPF_3 can be obtained from the reaction of PF_5 with borosilicate (Pyrex) glass which has been moistened with water. Phosphorus pentafluoride (270. mg, 2.1 mmole) was condensed into a 25 ml glass pressure vessel which had been moistened with water and dried by shaking in the air for several minutes. The stopcock was closed and the vessel was allowed to stand overnight at room temperature. The volatile material was then transferred into the vacuum system and distilled as follows:

$$RT \sim \underset{A}{-78^\circ} \sim -196^\circ \qquad \text{(2 times)}$$

$$RT \sim \underset{(B)}{-134^\circ} \sim \underset{(C)}{-196^\circ} \qquad \text{(3 times)}$$

Fractions (A) and (C) were discarded and fraction (B) retained: OPF_3 (129. mg, 1.24 mmole); mol. wgt. calcd. 103.5; confirmed by infrared spectrum.

Selenium - (Se, E. H. Sargent & Co.) used as obtained.

Sulfur - (S, Mallinckrodt) dried at 60° for 2 hours and used as obtained.

Telleurium - (Te, ASARCO, High Purity) used as obtained after powdering.

Trichlorosilyl tetracarbonyl Cobalt (I) - $Cl_3SiCo(CO)_4$ was obtained by resubliming a previously prepared ($Co_2(CO)_8$ + Cl_3SiH) and refrigerated sample. Approximately 5 gm of stored $Cl_3SiCo(CO)_4$ was transferred to a vacuum sublimer in an inert atmosphere. The sublimation apparatus was then evacuated to remove any higher volatiles that may have resulted from the decomposition of the stored product. After pumping for several minutes, the stopcock on the sublimation apparatus was closed and dry ice-acetone added to the cold finger. The sample was then allowed to sublime overnight.

The sublimed amber crystals had an infrared spectrum and mass spectrum in close agreement with the literature values.

Transition Metal Oxides - The following metal oxides were used as obtained.

CoO - (Vitro Laboratories)

Cr_2O_3 - (Research Organic/Inorganic Chemical Corporation)

CrO_3 - (Vitro Laboratories)

Fe_2O_3 - (Vitro Laboratories)

MoO_3 - (Vitro Laboratories)

NiO - (Vitro Laboratories)

RuO_2 - (Research Organic/Inorganic Chemical Corporation)

Na_2MoO_4 - (Merck, Reagent)

Na_2WO_4 - (Eimend and Amend, Reagent)

TaO_5 - (Research Organic/Inorganic Chemical Corporation)

TiO_2 - (Fisher Scientific - Amend & Eimend)

V_2O_5 - (Vitro Laboratories)

WO_3 - (Vitro Laboratories)

ZrO - (Vitro Laboratories)

Gold Tubing - Matthey Bishop, Inc., Malvern, Pa.

F. The High Pressure Interaction of Transition Metal Oxides with Phosphorus Trifluoride.

This section includes detailed information on the transition metal oxide phosphorus trifluoride reactions. The reactions are summarized in Table IIIA and IIIB.

Typical mass spectral data are reported in the appendices. These include PF_3 (Appendix C), phosphoryl fluorides (Appendix E) and Ni, W, and Mo - phosphorus trifluoride coordination compounds (Appendix F).

1. The Reaction of Nickel (II) Oxide with Phosphorus Trifluoride at High Pressure.

Summary: It was found that the reaction of NiO and PF_3 occurred readily at 4000 atmospheres and 300° for 12 hours according to the following equation,

$$NiO + 5\ PF_3 \rightarrow Ni(PF_3)_4 + OPF_3 \qquad (53)$$

Phosphorus trifluoride (195. mg., 2.21 mmole) was condensed into a gold tube which had been charged with NiO (20. mg., 0.267 mmole). The tube was sealed and held at 4000 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material distilled as follows:

$$RT \sim -63^\circ \sim -196^\circ \qquad \text{(3 times)}$$
$$\quad\ A \quad\ B$$

The following materials were identified:

$\underline{Ni(PF_3)_4}$: Fraction A. (33.3 mg., 0.081 mmole; 30.3% yield based on initial NiO; identified by infrared spectrum[83]; confirmed by mass spectrum).

$\underline{PF_3, OPF_3}$: Fraction B. (1.80 mmole gas out; infrared spectrum identical to that expected for a mixture of PF_3[59] and OPF_3[59]; OPF_3 (10.4 mg., 0.10 mmole); PF_3 (150. mg., 1.70 mmole)).

2. <u>The Reaction of Nickel (II) Oxide with Phosphorus Trifluoride at High Pressure in the Presence of Magnesium</u>.

<u>Summary</u>: It was found that the reaction of NiO and PF_3 in the presence of Mg occurred readily at 4000 atmospheres and 300° for 12 hours according to the following equation.

$$NiO + 5\ PF_3 \rightarrow Ni(PF_3)_4 + OPF_3 \qquad (54)$$

$$3\ OPF_3 + Mg \rightarrow MgF_2 + PF_3 + P_2O_3F_4 \qquad (55)$$

Phosphorus trifluoride (128. mg., 1.46 mmole) was condensed into a gold tube containing NiO (20. mg., 0.267 mmole) and Mg (24 mg., 1 mmole). The tube was sealed and held at 4000 atmospheres and 300° for 12 hours.

The tube was opened and the volatile material distilled as follows:

$$RT \sim \underset{(A)}{-78^\circ} \sim \underset{(B)}{-196^\circ} \qquad \text{(3 times)}$$

The following materials were identified:

$Ni(PF_3)_4$: Fraction A. (33.3 mg., 0.081 mmole), identified by infrared spectrum[83]; confirmed by mass spectrum[9]; a 30.3% yield based on initial NiO.

$P_2O_3F_4$: Fraction A. (contamination in mass spectrum, identified by the reaction of OPF_3 and Mg[8] at high pressure).

PF_3, OPF_3: Fraction B. (1.16 mmole gas out; 79.5% recovery based on initial PF_3; infrared spectrum consistent with a mixture PF_3[59] and OPF_3[59]; OPF_3 (10.4 mg., 0.10 mmole); PF_3 (93.3 mg., 1.06 mmole)).

3. The Reaction of Nickel (II) Oxide with Phosphorus Trifluoride in the Presence of Magnesium.

Summary: It was found that the reaction of NiO and PF_3 in the presence of Mg occurred readily at 100 atmospheres and 300° for 12 hours according to the equation,

$$NiO + 5\ PF_3 \rightarrow Ni(PF_3)_4 + OPF_3 \qquad (56)$$

$$3\ OPF_3 + Mg \rightarrow PF_3 + P_2O_3F_4 + MgF_2 \qquad (57)$$

Phosphorus trifluoride (81.4 mg., 0.925 mmole) was condensed into a gold tube containing NiO (20. mg., 0.267 mmole) and Mg (24. mg., 1 mmole). The tube was sealed and held at 100 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material distilled as follows:

$$RT \sim -78^\circ \sim -196^\circ \qquad \text{(2 times)}$$
$$\text{(A)} \quad \text{(B)}$$

The following materials were identified:

$Ni(PF_3)_4$: Fraction A. (32.8 mg., 0.08 mmole); identified by infrared spectrum[83]; confirmed by mass spectrum[9]; 30% yield based on initial NiO.

PF_3, OPF_3: Fraction B. (0.60 mmole gas out; 65% recovery based on initial PF_3; infrared spectrum consistent with a mixture of PF_3[59] and OPF_3[59]; OPF_3 (10.4 mg., 0.10 mmole); PF_3 (44. mg., 0.50 mmole)).

4. The Reaction of Molybdenum VI Oxide with Phosphorus Trifluoride at High Pressure.

Summary: It was found that MoO_3 and PF_3 reacted readily at 4000 atmospheres and 300° for 12 hours according to the following equation,

$$MoO_3 + 3\ PF_3 \rightarrow Mo + 3\ OPF_3 \qquad (58)$$

Phosphorus trifluoride (109. mg., 1.24 mmole) was condensed into a gold tube containing MoO_3 (20 mg., 0.13 mmole). The tube was sealed and held at 4000 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material trapped at -196°.

The following material was identified:

PF_3 and OPF_3: (0.95 mmole out; 76% recovery; infrared spectrum equivalent to that expected for a mixture of PF_3[59] and OPF_3[59]; OPF_3 (31.2 mg., 0.30 mmole); PF_3 (57.2 mg., 0.65 mmole); loss of volatiles apparently due to the formation of $P_2O_3F_4$ or other polymeric $(POF)_n$[171].

5. The Reaction of Molybdenum VI Oxide with Phosphorus Trifluoride at High Pressure in the Presence of Magnesium.

Summary: It was found that MoO_3 and PF_3 reacted readily in the presence of Mg at 4000 atmospheres and 300° for 12 hours according to the following equation,

$$MoO_3 + PF_3 \rightarrow Mo(PF_3)_6 + 3\ OPF_3 \qquad (59)$$

$$3\ OPF_3 + Mg \rightarrow MgF_2 + P_2O_3F_4 + PF_3 \qquad (60)$$

Phosphorus trifluoride (108. mg., 1.23 mmole) was condensed into a gold tube containing MoO_3 (20 mg., 0.12 mmole) and Mg (24 mg., 1 mmole). The tube was sealed and held at 4000 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material distilled as follows:

RT ∿ -131° ∿ -196° (1 time)
↓ (A)
∿ -63° ∿ -196° (1 time)
(A)

The following material was identified:

$\underline{Mo(PF_3)_6}$: Fraction B. (31.2 mg., 0.05 mmole); identified by infrared spectrum[81]; confirmed by mass spectrum[10]; a 38% yield based on initial MoO_3.

$\underline{P_2O_3F_4}$: Fraction B. (unknown contamination in mass spectrum, later identified by the reaction of OPF_3 and Mg[8]).

$\underline{PF_3 \text{ and } OPF_3}$: Fraction A. (1.07 mmole gas out; 87% recovery; identified by infrared spectrum[59]; OPF_3 (31.2 mg., 0.30 mmole); PF_3 (67.8 mg., 0.77 mmole)).

6. The Attempted Reaction of Molybdenum VI Oxide with Phosphorus Trifluoride.

Summary: It was found that MoO_3 and PF_3 did not react at 100 atmospheres and 300° in the presence of Mg for 12 hours.

Phosphorus trifluoride (108. mg., 1.23 mmole) was condensed into

a gold tube containing MoO_3 (20 mg., 0.13 mmole) and Mg (24. mg., 1 mmole). The tube was sealed and held at 100 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material trapped at -196°.

The following material was identified:

PF_3: (identified by infrared spectrum[59]; 83.6 mg., 0.95 mmole; 86.3% recovery).

7. The Reaction of Tungsten (VI) Oxide with Phosphorus Trifluoride at High Pressure.

Summary: It was found that WO_3 and PF_3 reacted readily at 4000 atmospheres and 300° for 12 hours according to the following equation,

$$WO_3 + 3\ PF_3 \rightarrow W + 3\ OPF_3 \qquad (61)$$

Phosphorus trifluoride (100. mg., 1.14 mmole) was condensed into a gold tube containing WO_3 (35 mg., 0.15 mmole). The tube was sealed and held at 4000 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material trapped at -196°.

The following material was identified:

PF_3 and OPF_3: (0.91 mmole out; 80% recovery; infrared spectrum identical with that expected for a mixture of PF_3[59] and OPF_3[59]; OPF_3 (31.2 mg., 0.30 mmole); PF_3 (57.7 mg., 0.61 mmole); loss of volatile material apparently due to the formation of $P_2O_3F_4$).

8. The Reaction of Tungsten VI Oxide with Phosphorus Trifluoride in the Presence of Magnesium.

Summary: It was found that WO_3 and PF_3 reacted readily in the presence of Mg at 4000 atmospheres and 300° for 12 hours according

to the following equation,

$$WO_3 + PF_3 \rightarrow W(PF_3)_6 + 3\ OPF_3 \quad (62)$$

$$3\ OPF_3 + Mg \rightarrow P_2O_3F_4 + PF_3 + MgF_2 \quad (63)$$

Phosphorus trifluoride (81.0 mg., 0.90 mmole) was condensed into a gold tube containing WO_3 (34.7 mg., 0.15 mmole) and Mg (24 mg., 1 mmole). The tube was sealed and held at 4000 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material distilled as follows:

RT ∿ -131°	∿ -196°	(1 time)
↓	(A)	
∿ -23°	∿ -196°	(1 time)
(B)	(A)	

The following material was identified:

$W(PF_3)_6$: Fraction B. (25.5 mg., 0.04 mmole); identified by infrared spectrum[86]; confirmed by mass spectrum[11]; 27% yield based on initial WO_3.

$P_2O_3F_4$: Fraction B. (unknown contamination in mass spectrum, identified later by reaction of OPF_3 and Mg[8]).

PF_3 and OPF_3: Fraction A. (0.566 mmole gas out; 62.0% recovery; identified by infrared spectrum[59]; OPF_3 (25. mg., 0.24 mmole); PF_3 (29. mg., 0.33 mmole)).

9. The Attempted Reaction of Tungsten (VI) Oxide with Phosphorus Trifluoride at High Pressure.

Summary: It was found that WO_3 and PF_3 did not react at 100 atmospheres and 300° in the presence of Mg for 12 hours.

Phosphorus trifluoride (100. mg., 1.14 mmole) was condensed into a gold tube containing WO_3 (35. mg., 0.15 mmole) and Mg (24 mg., 1 mmole). The tube was sealed and held at 100 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material trapped at -196°.

The following material was identified:

PF_3: (identified by infrared spectrum[59]; 84 mg., 0.96 mmole; 94.1% recovery).

10. The Reaction of Iron (III) Oxide with Phosphorus Trifluoride at High Pressure.

Summary: It was found that Fe_2O_3 and PF_3 reacted readily at 4000 atmospheres and 300° for 12 hours according to the following equation,

$$Fe_2O_3 + XPF_3 \rightarrow Fe_2O_{(3-x)} + XOPF_3 \qquad (64)$$

Phosphorus trifluoride (66.2 mg., 0.752 mmole) was condensed into a gold tube containing Fe_2O_3 (30.0 mg., 0.18 mmole). The tube was sealed and held at 4000 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material trapped at -196°.

The following material was identified:

PF_3 and OPF_3: (0.724 mmole out; 96.2% recovery; infrared spectrum identical with that expected for a mixture of PF_3[59] and OPF_3[59]; OPF_3 (12.5 mg., 0.12 mmole); PF_3 (52.8 mg., 0.60 mmole)).

11. The Reaction of MO_x with Phosphorus Trifluoride in the Presence of Magnesium at High Pressure.

Summary: It was found that MO_x (where M = Cr, Ta, Ru, Os, Zr, V,

Ti, Fe, Co) and PF_3 reacted readily at 4000 atmospheres and 300° for 12 hours according to the following equation,

$$MO_x + x\ PF_3 \rightarrow M + x\ OPF_3 \tag{65}$$

$$3\ OPF_3 + Mg \rightarrow MgF_2 + P_2O_3F_4 + PF_3 \tag{66}$$

As shown in Table IIIA PF_3 (88 mg., 1 mmole) was condensed into a gold tube containing MO_x and Mg (24 mg., 1 mmole). The tube was sealed and held at 4000 atmospheres and 300° for 12 hours.

The tube was opened and volatile material distilled as follows:

$$RT \sim -63° \sim -196°$$
$$(A)$$

The following material was identified:

$\underline{P_2O_3F_4}$: Fraction A. (unknown product, identified by reaction of OPF_3 and Mg[4]; HO_2PF_2 identified by infrared[20] and mass spectrum[8] (hydrolysis product).

$\underline{PF_3 \text{ and } OPF_3}$: Fraction B. (identified by infrared spectrum[59]).

In Table IIIA, the number in parenthesis alongside MO_x indicates the number of times each reaction was attempted in the series of reactions. Before final identification of the $P_2O_3F_4$, the solid residue in the Au tube was known to fume in air and to be caked by an oily liquid, all of which is inconsistent with the generally very unstable, reasonably volatile $P_2O_3F_4$ and its hydrolysis products.

TABLE IIIA

Reaction of MO_x with PF_3 at 4000 ATM and 300°

	Reactants[a]		Products[a]	
	MO_x + Mg	PF_3	(OPF_3) (PF_3)	$P_2O_3F_4$ (calcd.)
1.	Cr_2O_3 (9)	1.08	(0.044) (0.392)	0.32
2.	CrO_3 (2)	1.16	(0.125) (0.700)	0.17
3.	RuO_2 (2)	1.41	(0.088) (0.794)	0.26
4.	Na_2WO_4 (1)	1.35	(0.070) (0.624)	0.33
5.	Na_2MoO_4 (1)	1.44	(0.070) (0.632)	0.37
6.	ZrO (1)	1.26	(0.040) (0.872)	0.18
7.	V_2O_5 (1)	1.08	(0.061) (0.572)	0.22
8.	TiO_2 (1)	0.966	(0.081) (0.753)	0.07
9.	Fe_2O_3 (4)	1.18	(0.071) (0.631)	0.24
10.	CoO (1)	0.966	(0.021) (0.645)	0.15
11.	OsO_4[b] (1)	1.24	(0.080) (0.764)	0.20
12.	TaO_5 (1)	1.24	(0.062) (0.534)	0.32
13.	MnO (1)	1.03	(0.020) (0.765)	0.12
14.	RuO_2[b] (1)	1.41	(0.044) (0.838)	0.30

[a] The quantities are given in millimoles.

[b] Reacted at 4000 atmospheres and 200°.

TABLE IIIB

Reaction of MO_x with PF_3 at 300°

#	Reactant[a] MO_x	Mg	PF_3	Pressure[b]	Products[a] $M(PF_3)_x$	$(OPF_3)(PF_3)$
1	NiO	---	2.21	4000	0.08	(0.10)(1.70)
2	NiO	1.0	1.46	4000	0.06	(0.10)(1.06)
3	NiO	1.0	0.925	100	0.08	(0.10)(0.50)
4	MoO_3	---	1.24	4000	----	(0.30)(0.65)
5	MoO_3	1.0	1.23	4000	0.02	(0.30)(0.77)
6	MoO_3	1.0	1.10	100	----	(0.0)(0.95)
7	WO_3	---	1.14	4000	----	(0.30)(0.61)
8	WO_3	1.0	0.90	4000	0.03	(0.24)(0.33)
9	WO_3	1.0	1.02	100	----	(0.0)(0.96)
10	Fe_2O_3	---	0.752	4000	----	(0.12)(0.60)

[a] The quantities are given in millimoles.

[b] Pressure is given in atmospheres.

G. The High Pressure Interaction of the Group VIA Elements with Phosphorus Trifluoride and the Interaction of Magnesium with P-O-F Compounds.

This section includes detailed information on the Group VIA - phosphorus trifluoride interactions with and without magnesium. The reactions are summarized in Table IV.

Typical mass spectral data are reported in the appendices. These include PF_3 (Appendix C) and the phosphoryl fluoride (Appendix E).

1. Low Pressure Synthesis of Phosphoryl Fluoride.

Summary: The reaction of PF_5 and O_2 in the presence of Mg metal was found to occur readily at 300° and 0.1 atmosphere pressure according to the following equation,

$$PF_5 + 1/2\ O_2 + Mg \rightarrow OPF_3 + MgF_2 \qquad (67)$$

Phosphorus pentafluoride (1.71 mmole, 126 mg) was condensed into the cold finger of a 1 liter glass reaction vessel (Figure 4) in which had been placed Mg (0.5 mg.). The vacuum line and manometer were purged with O_2 and the O_2 (48 mg., 1.5 mmole) was condensed as a liquid into the reactor at -196°.

The stopcock was closed and the cold finger was heated at 300° with an electrical furnace for 20 minutes. The furnace was removed from the cold finger and when the reaction vessel reached room temperature the mixture was cooled to -196°.

The vessel was then opened to a -196° trap on the vacuum line. The excess O_2 was pumped off for several minutes until no more pressure could be observed on the manometer. The liquid nitrogen bath was

removed from the cold finger and the volatile material collected on the vacuum line with intermittant pumping. The volatile material was distilled as follows:

$$\underset{(A)}{RT} \sim -95^\circ \sim \underset{(B)}{-196^\circ} \qquad \text{(3 times)}$$

The following material was identified:

ow Volatiles: Fraction A. (Some small amount of material collected and discarded).

OPF_3: Fraction B. (1.59 mmoles, 165.3 mg., mol. wgt. calcd. 103.97, found 104.1; 80% yield based on the initial amount of PF_5; confirmed by infrared[59] and mass spectrum[150]).

2. High Pressure Synthesis of Phosphoryl Fluoride.

Summary: The reaction of PF_3 and O_2 at 4000 atmospheres and at 300° for 12 hours was observed to occur, forming OPF_3 in an 86% yield according to the following equation,

$$2\ PF_3 + O_2 \rightarrow 2\ OPF_3 \qquad (68)$$

Phosphorus trifluoride (64.9 mg., 0.738 mmoles) was condensed into a gold tube. The calibrated vacuum line and manometer were purged with oxygen and the oxygen (32.0 mg., 1 mmole) was condensed into the gold tube with the phosphorus trifluoride. The tube was sealed and held at 4000 atmospheres and 300° for 12 hours.

The gold tube was opened and the excess oxygen was removed by pumping the volatile substances through two traps cooled to -196°.

$$\underset{(A)}{RT} \sim -196^\circ \qquad \text{(with pumping)}$$

The following materials were identified:

PF_3 and OPF_3: Fraction A. (mol. wgt. calcd. 101.7; 85.6% yield based on mixed molecular weight; mixture of products confirmed by infrared spectrum[59] and mass spectrum[150] (m/e = 104 for OPF_3, m/e = 88 for PF_3 with appropriate cracking patterns as observed for pure samples); OPF_3 (65.7 mg., 0.632 mmole); PF_3 (10.8 mg., 0.123 mmole).

3. Attempted High Pressure Synthesis of Phosphoryl Fluoride.

Summary: It was found that PF_3 did not react with O_2 at 4000 atmospheres and at 25° within 12 hours.

Phosphorus trifluoride (84.8 mg., 0.964 mmole) was condensed in a gold tube. The vacuum line was purged with oxygen and an excess (3 mmoles, 96 mg.) was condensed into the gold tube. The tube was sealed and pressured at 4000 atmospheres and 25° for 12 hours.

The gold tube was opened and the excess oxygen was removed by pumping the volatile mixture through two traps cooled to -196°.

$$\underset{(A)}{RT \sim -196°} \qquad \text{(with pumping)}$$

The following material was identified:

PF_3: Fraction A. (identified by infrared spectrum[50] and confirmed by molecular weight; mol. wgt. calcd. 87.97, found 86.0; 98% recovery of PF_3 (83.2 mg., 0.945 mmole).

4. High Pressure Synthesis of μ-Oxo-bisdifluorophosphoryl.

Summary: The reaction of PF_3 and O_2 in the presence of Mg at 4000 atmospheres and at 300° for 12 hours was observed to occur, forming OPF_3 and HO_2PF_2 and H_2O_3PF according to the following equation,

$$PF_3 + O_2 + \overset{H_2O}{} \quad OPF_3 + HO_2PF_2 + H_2O_3PF \qquad (69)$$

Phosphorus trifluoride (84.8 mg., 0.946 mmoles) was condensed into a gold tube which contained Mg (24 mg., 1 mmole). The calibrated vacuum line and manometer were purged with O_2, then O_2 (64 mg., 2 mmoles) was condensed into the gold tube and the tube was sealed. It was then pressured to 4000 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material was distilled as follows:

RT ∿ -63.5° ∿ -196° (3 times)

The following materials were identified:

$\underline{HO_2PF_2}$, $\underline{H_2O_3PF}$: Fraction A. (86% yield on the basis of OPF_3 passing this fraction; expected hydrolysis product of $P_2O_3F_4$ and H_2O (from Au and opener); identified by infrared[20], confirmed by mass spectrum[8]; 9.813 mmoles, HO_2PF_2 and H_2O_3PF).

$\underline{OPF_3}$: Fraction B. (14.1 mg., 0.135 mmoles, identified by infrared spectrum[50]).

5. <u>High Pressure Synthesis of μ-Oxo-bisdifluorophosphoryl</u>.

<u>Summary</u>: The reaction of PF_3 and O_2 in the presence of Mg at 4000 atmospheres and 300° for 12 hours was observed to occur, forming OPF_3 and $P_2O_3F_4$ according to the following equation,

$$3\ PF_3 + 2\ O_2 + Mg \rightarrow OPF_3 + P_2O_3F_4 + MgF_2 \qquad (70)$$

Due to the highly water sensitive nature of $P_2O_3F_4$, extreme precautions were taken to eliminate all H_2O. The gold opener was heated to 500° with a CH_4/O_2 torch and cooled in a drying oven. The gold tubing was heated red hot (900°) before loading the sample. The gold became extremely malleable and soft after heating and vapors were

observed to diffuse out of the open end, indicating the presence of H_2O.

Phosphorus trifluoride (88.0 mg., 1.00 mmole) was condensed into a gold tube which contained Mg (24 mg., 1 mmole). The vacuum line and manometer were purged with O_2, the O_2 (4.8 mg., 1.5 mmole) was condensed into the gold tube. The tube was sealed and pressurized to 4000 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material was distilled as follows:

$$\underset{}{RT} \sim \underset{(A)}{-63.5^\circ} \sim \underset{(B)}{-196^\circ} \qquad (3 \text{ times})$$

The following materials were identified:

$\underline{P_2O_3F_4, HO_2PF_2 \text{ \& } H_2O_3PF}$: Fraction A. (mass spectrum[8] identical to that expected for this mixture, m/e's at 186, 167, 102, 100; sample reacts with KBr, so infrared not feasible; fluorophosphoric acid products must be due to condensed H_2O on the gold tube, typical of $P_2O_3F_4$; 63.2 mg., 0.34 mmole; 68% yield on the basis of initial PF_3).

$\underline{OPF_3}$: Fraction B. (32.6 mg., 0.314 mmole) identified by infrared spectrum[59].

6. Low Pressure Synthesis of μ-Oxo-bisdifluorophosphoryl.

Summary: The reaction of PF_5 and O_2 in the presence of Mg was found to occur readily at 300° and 1 atmosphere pressure according to the following equation,

$$PF_5 + 1/2\ O_2 + Mg \rightarrow OPF_3 + MgF_2 \qquad (71)$$

$$2\ OPF_3 + 1/2\ O_2 + Mg \rightarrow P_2O_3F_4 + MgF_2 \qquad (72)$$

Phosphorus pentafluoride (1.5443 g, 12.25 mmole) was condensed

into the cold finger of a 1 liter glass reaction vessel (Figure 4) in which Mg (1.622 g, 62.6 mmoles) had been placed. The vacuum line and manometer were purged with O_2 and then O_2 (320 mg., 10 moles) was condensed as a liquid into the reactor at -196°.

The stopcock was closed and the cold finger was heated at 300° with an electric furnace for 2.5 hours. The furnace was removed from the cold finger and when the reaction vessel reached room temperature the mixture was cooled to -196°. The vessel was then opened to a -196° trap on the vacuum line. The excess O_2 was pumped off through the -196° trap for several minutes until no more pressure could be observed on the manometer. The liquid nitrogen bath was removed from the cold finger and the volatile material collected on the vacuum line with intermittant pumping. The volatile material was distilled as follows:

$$\text{RT} \sim -96° \sim -196° \quad \text{(A)}$$

$$\downarrow$$

$$\text{RT} \sim -96° \sim -196° \quad \text{(B)} \quad \text{(C)}$$

The following material was identified:

$\underline{P_2O_3F_4, HO_2PF_2}$: Fraction B. (330 mg., 1.77 mmole) indicated by infrared[20]; confirmed by mass spectrum[8]; HO_2PF_2 present due to the high reactivity of $P_2O_3F_4$ (see introduction).

$\underline{OPF_3}$: Fraction C. (430. mg., 4.13 mmole) identified by infrared[59]; confirmed by mass spectrum[150].

$\underline{OPF_3, SiF_4, (SiF_3)_2O}$: Fraction A. Determined by infrared spectrum[59]; common products for the PF_5 reactions in glass.

A white flakey nonvolatile solid was observed on the sides of the glass coldfinger. This white flakey powder, did not fume in air, very

soluble in aqueous solution (pH ≈1), is very consistent with polymeric $(PO_2F)_n$ as described by Wannagat and Rademachers[171] in their silent electrical discharge reaction of PF_3 and O_2.

7. High Pressure Synthesis of Thiophosphoryl Fluoride.

Summary: The reaction of PF_3 and S was found to occur readily at 4000 atmospheres and 300° according to the following equation

$$PF_3 + S \rightarrow SPF_3 \qquad (73)$$

Phosphorus trifluoride (77.0 mg., 0.875 mmole) was condensed into a gold tube containing S (320 mg., 10 mmole) that had been dried at 100° for 4 hours. The tube was sealed and held at 4000 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material trapped at -196°.

The following material was identified:

SPF_3 and PF_3: (identified by infrared[59,40], confirmed by mass spectrum[150,79]; ave. mol. wgt. found 118.6, corresponds to 95.8% SPF_3 and 4.2% PF_3; SPF_3 (101. mg., .838 mmole); PF_3 (3.2 mg., 0.037 mmole).

8. Low Pressure Synthesis of Thiophosphoryl Fluoride.

Summary: The reaction of PF_3 and S was found to occur at 200 atmospheres and at 300° according to the following equation.

$$S + PF_3 \rightarrow SPF_3 \qquad (74)$$

Phosphorus trifluoride (93.36 mg., 1.061 mmole) was condensed into a gold tube containing S (320 mg., 10 mmole) that had been dried at 100° for 4 hours. The tube was sealed and held at 200 atmospheres and at 300° for 12 hours.

The gold tube was opened and the volatile material trapped at -196°. The following material was identified:

SPF_3 and PF_3: (identified by infrared[59,40], confirmed by mass spectrum[150,79]; ave. mol. wgt. found 104.9, corresponds to 52.9% SPF_3 and 47.1% PF_3; SPF_3 (0.561 mmole, 67.3 mg.); PF_3 (0.500 mmole, 44.0 mg.)).

9. High Pressure Synthesis of Thiophosphoryl Fluoride.

Summary: The reaction of PF_3 and S was found to occur at 4000 atmospheres and at 200°.

$$S + PF_3 \rightarrow SPF_3 \qquad (75)$$

Phosphorus trifluoride (103.2 mg., 1.173 mmole) was condensed into a gold tube containing S (320 mg., 10 mmole) that had been dried at 100° for 4 hours. The tube was sealed and held at 4000 atmospheres and at 200° for 12 hours.

The gold tube was opened and the volatile material trapped at -196°. The following material was identified:

PF_3 and SPF_3: (identified by infrared spectrum[59,40], confirmed by mass spectrum[159,79]; mol. wgt. out 92.28, corresponds to 86.6% PF_3, 13.4% SPF_3; PF_3 (89.8 mg., 1.02 mmole); SPF_3 (18.8 mg., 0.147 mmole).

10. High Pressure Synthesis of Selenophosphoryl Fluoride.

Summary: The reaction of PF_3 and Se was found to occur at 4000 atmospheres and 300° for 12 hours according to the following reaction,

$$Se + PF_3 \rightarrow SePF_3 \qquad (76)$$

Phosphorus trifluoride (97.0 mg., 1.10 mmole) was condensed into a gold tube containing Se (78 mg., 1 mmole) powder. The tube was

sealed and held at 4000 atmospheres and at 300° for 12 hours.

The gold tube was opened and the volatile material distilled as follows,

$$RT \sim -95^\circ \sim -196^\circ \qquad \text{(2 times)}$$
$$\text{(A)} \quad \text{(B)}$$

The following material was identified:

$SePF_3$ and OPF_3: Fraction A. indicated by infrared[59]; confirmed by mass spectrum[159,7]; the OPF_3 could be from SeO_2 or reaction of $SePF_3$ with water from the gold tube; 50% yield based on initial PF_3; $SePF_3$ (83.5 mg., 0.55 mmole).

PF_3 and OPF_3: Fraction B. (determined by infrared spectrum[59]; PF_3 (44.0 mg., 0.50 mmole); OPF_3 (5.2 mg., 0.05 mmole).

Several attempts were made to obtain an infrared spectrum of $SePF_3$, but none were successful. The compound decomposed in the infrared cell and in the vacuum line, leaving a reddish brown, nonvolatile, inert solid behind.

11. High Pressure Reaction of Tellurium with Phosphorus Trifluoride.

Summary: The reaction of PF_3 and Te at 4000 atmospheres and 300° did not occur after 12 hours.

$$Te + PF_3 \rightarrow \text{No Reaction} \qquad (77)$$

Phosphorus trifluoride (126.1 mg., 1.433 mmole) was condensed into a gold tube containing Te (120 mg., 1 mmole). The tube was sealed and held at 4000 atmospheres and at 300° for 12 hours.

The gold tube was opened and the volatile material distilled as

follows:

$$\underset{(A)}{RT} \sim -95^\circ \sim \underset{(B)}{-196^\circ}$$

The following material was identified:

PF_3: Fraction B. (identified by infrared spectrum[59], quantitative recovery of PF_3 (126. mg., 1.43 mmole)).

H_2O: Fraction A. (identified by mass spectrum)[147]. The water is due to ice on the outside of the gold tube, which forms as the tube, cooled to -196°, is exposed to the air.

12. High Pressure Synthesis of Thiophosphoryl Fluoride in the Presence of Magnesium.

Summary: The reaction of PF_3 and S in the presence of Mg was found to occur readily at 4000 atmospheres and 300° according to the following equation,

$$PF_3 + S + Mg \rightarrow SPF_3 \qquad (78)$$

Phosphorus trifluoride (94.5 mg., 1.07 mmole) was condensed into a gold tube containing S (320 mg., 10 mmole) and Mg (24 mg., 1 mmole). The tube was sealed and held at 4000 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material trapped at -196°.

The following volatile products were identified:

SPF_3 and PF_3: (identified by infrared spectrum[40,59]; confirmed by mass spectrum[79,159]; ave. mol. wgt. found 101.4, corresponds to 82% SPF_3 and 18% PF_3; 102% recovery on basis of initial PF_3; SPF_3 (105. mg., 0.877 mmole); PF_3 (17.0 mg., 0.193 mmole).

13. High Pressure Synthesis of Selenophosphoryl Fluoride at 500°.

Summary: The reaction of PF_3 and Se was observed to occur readily at 500° along with corresponding alloying of the Au tube, viz.

$$Se + PF_3 \rightarrow SePF_3 \quad (79)$$

$$Se + Au \rightarrow Au\text{-}Se \text{ (alloy)} \quad (80)$$

Phosphorus trifluoride (97.0 mg., 1.102 mmole) was condensed into a gold tube containing Se (87. mg., 1.1 mmole). The tube was sealed and held at 4000 atmospheres and 500° for 12 hours.

The gold tube was opened and the volatile material distilled as follows:

$$RT \sim -95° \sim -196°$$
$$(A) \quad (B)$$

The following materials were identified:

$SePF_3$, OPF_3: Fraction A. Confirmed by mass spectrum[7,150]; the tube burst in the opener and some volatiles pumped away, but a very good $SePF_3$ yield; $SePF_3$ (108. mg., 0.65 mmole).

PF_3: Fraction B. (39.6 mg., 0.45 mmole); identified by infrared spectrum[1].

14. High Pressure Reaction of Tellurium with Phosphorus Trifluoride.

Summary: The reaction of PF_3 and Te did not occur at 4000 atmospheres and 500° after 12 hours.

Phosphorus trifluoride (154 mg., 1.2 mmole) was condensed into

a gold tube containing Te (120 mg., 1 mmole). The tube was sealed and held at 4000 atmospheres and 500° for 12 hours.

The Au tube burst in the autoclave and no products were isolated. A Au-Te allow was observed as with the Se.

15. The Reaction of Oxygen, Sulfur and Selenium with Phosphorus Trifluoride at One Atmosphere and 300°.

Summary: It was found that PF_3 and O_2, S or Se did not react at 300° under autogenous pressure for four hours.

Phosphorus trifluoride (176. mg., 2 mmoles) was condensed into the cold finger of a one liter pyrex glass reaction vessel at -196°. The reactants were allowed to warm to room temperature and then the cold finger was heated to 300° with a resistance furnace. After four hours, the furnace was withdrawn and the cold finger cooled to -196°.

The volatiles were then transferred to the vacuum line at -196° and analyzed as previously indicated in this section.

No reaction was observed in either of the three reactions with quantitative recovery of the PF_3.

16. Low Pressure Reaction of Magnesium Oxide and Phosphorus Pentafluoride.

Summary: The reaction of PF_5 and MgO was found to occur at 300° and 1 atmosphere according to the following equation,

$$PF_5 + MgO \rightarrow MgF_2 + OPF_3 \qquad (81)$$

Phosphorus pentafluoride (252. mg., 2.0 mmole) was condensed into the cold finger of a one liter glass reaction vessel (Figure 4) which

contained MgO (160 mg., 4.0 mmole).

The stopcock was closed and the cold finger heated at 300° and autogenous pressure with a resistance furnace for 2 hours. The furnace was removed from the cold finger and the cold finger was cooled to -196°. The vessel was then opened to a -196° trap on the vacuum line, the -196° bath was removed from the reactor vessel cold finger and the volatile material collected on the vacuum line.

The following material was identified:

OPF_3 and PF_5: (identified by infrared[59]; 46% conversion to OPF_3, based on mixed molecular weight; PF_5 (136. mg., 1.08 mmole); OPF_3 (95.7 mg., 0.92 mmole)).

17. Low Pressure Reaction of Magnesium Oxide and Phosphoryl Fluoride.

Summary: The reaction of OPF_3 and MgO was found to occur readily at 300° and 1 atmosphere according to the following equation,

$$2\ OPF_3 + MgO \rightarrow MgF_2 + P_2O_3F_4 \qquad (82)$$

Phosphoryl fluoride (212. mg., 2.04 mmole) was condensed into the cold finger of a one liter reaction vessel (Figure 4) which contained MgO (160 mg., 4.0 mmole).

The stopcock was closed and the cold finger heated at 300° with a resistance furnace for 2 hours. The furnace was removed from the cold finger and the cold finger was cooled to -196°. The vessel was then opened to a -196° trap on the vacuum line, the -196° bath was removed from the reactor vessel cold finger and the volatile material collected on the vacuum line.

The volatile material was distilled as follows:

$$RT \sim -63° \sim -196° \qquad \text{(2 times)}$$

The following material was identified:

$P_2O_3F_4$: Fraction A. (53.2 mg., 0.286 mmole; indicated by infrared[20]; confirmed by mass spectrum[8]; yield of 14% based on initial amount of OPF_3).

OPF_3: Fraction B. (1.46 mmoles, 152. mg.; identified by infrared[59]; confirmed by mass spectrum[150]).

18. High Pressure Reaction of Phosphoryl Fluoride and Magnesium.

Summary: The reaction of OPF_3 and Mg was observed to occur at 4000 atmospheres and 300° with a 20% yield according to the equation,

$$OPF_3 + Mg \rightarrow P_2O_3F_4 + MgF_2 \qquad (83)$$

Phosphoryl fluoride (165. mg., 1.59 mmole) was condensed into a gold tube containing Mg (24 mg., 1.0 mmole). The gold tube was sealed and held at 4000 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material distilled as follows:

$$RT \sim \underset{(A)}{-63°} \sim \underset{(B)}{-196°} \qquad \text{(2 times)}$$

The following material was identified:

$P_2O_3F_4$: Fraction A. (60. mg., 0.32 mmole; indicated by infrared[20]; confirmed by mass spectrum[8]; a 20% yield based on the initial amount of OPF_3).

OPF_3: Fraction B. (94.6 mg., 0.901 mmole; identified by infrared

TABLE IV

Summary of PF_x - Group VIA Reactions

#	Reactant[a]	Mg	PF_x	(P/T)[b]	Products
1	O_2(1.5)	20.	PF_5(1.71)	1/300°	OPF_3(1.59)
2	O_2(1.0)		PF_3(0.738)	4000/300°	OPF_3(0.632), PF_3(0.106)
3	O_2(3.0)		PF_3(0.964)	4000/25°	PF_3(0.964)
4	O_2(1.5)	1.0	PF_3(0.946)	4000/300°	OPF_3(0.135), HO_2PF_2(0.81)
5	O_2(1.5)	1.0	PF_3(1.00)	4000/300°	OPF_3(0.314), $P_2O_3F_4$(0.343)
6	O_2(10.0)	62.6	PF_5(12.25)	1/300°	OPF_3(4.13), $P_2O_3F_4$(1.77)
7	S (10.0)		PF_3(0.875)	4000/300°	SPF_3(0.838), PF_3(0.037)
8	S (10.0)		PF_3(1.061)	200/300°	SPF_3(0.561), PF_3(0.500)
9	S (10.0)		PF_3(1.173)	4000/200°	SPF_3(0.157), PF_3(1.016)
10	Se(1.0)		PF_3(1.10)	4000/300°	$SePF_3$(0.55), PF_3(0.55)
11	Te(1.0)		PF_3(1.433)	4000/300°	PF_3(1.431)
12	S (10.0)	1.0	PF_3(1.07)	4000/300°	SPF_3(0.88), PF_3(0.19)
13	Se(1.0)		PF_3(1.102)	4000/500°	$SePF_3$(0.65), PF_3(0.45)
14	Te(1.0)		PF_3(1.19)	4000/500°	PF_3(Lost), (Au Te alloy)
15	O_2,S,Se(1.0)		PF_3(2.0)	1/300°	PF_3(2.0)
16	MgO(4.0)		PF_5(2.0)	1/300°	OPF_3(0.92), PF_5(1.08)
17	MgO(4.0)		OPF_3(2.04)	1/300°	OPF_3(1.46), $P_2O_3F_4$(0.29)
18	-------	1.0	OPF_3(1.59)	4000/300°	OPF_3(0.901), $P_2O_3F_4$(0.32)
19	O_2(2.0)	0.5	PF_3(2.0)	1/300°	PF_3(2.0)

[a] The quantities are given in millimoles.

[b] Pressure is given in atmospheres, temperature in °C.

spectrum[59]).

19. The Attempted Reaction of Phosphorus Trifluoride and Oxygen at One Atmosphere.

Summary: The reaction of PF_3 and O_2 did not occur in the presence of Mg at 0.1 atmosphere and 300° for 1 hour.

$$PF_3 + O_2 + Mg \rightarrow \text{No Reaction} \qquad (84)$$

Phosphorus trifluoride (176. mg., 2.0 mmole) was condensed into the cold finger of a one liter glass reaction vessel (Figure 4) in which had been placed Mg (0.5 gm). The vacuum line and manometer were pruged with O_2 and then O_2 (64 mg., 2.0 mmole) was condensed as a liquid into the reactor at -196°. The stopcock was closed and the cold finger was heated at 300° under autogenous pressure for 1 hour. The furnace was removed from the cold finger and the cold finger was cooled to -196°. The vessel was then opened to a -196° trap on the vacuum line. The excess O_2 was pumped off for several minutes until no more pressure could be observed on the manometer. The liquid nitrogen bath was removed from the cold finger and the volatile material collected on the vacuum line at -196° with intermittant pumping.

The following material was identified:

PF_3: (176. mg., 2 mmole; identified by infrared spectrum[59]; confirmed by mass spectrum[150]).

H. The High Pressure Hydrolysis of the Fluorochloromethanes.

This section includes detailed information on the interaction on the high pressure hydrolysis of fluorochloromethanes. The reactions

are summarized in Table V.

Typical mass spectral data of the fluorochloromethanes is reported in Appendix D.

1. The High Pressure Reaction of Carbon Tetrachloride and Water.

Summary: The reaction of CCl_4 and H_2O at 4000 atmospheres and 300° was found to occur readily within 12 hours as given by the equation,

$$CCl_4 + 2\ H_2O \rightarrow CO_2 + 4\ HCl \qquad (85)$$

Carbon tetrachloride (154 mg., 1.00 mmole) was transferred into a gold tube containing H_2O (119. mg., 6.7 mmole). The tube was evacuated, sealed and held at 4000 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material trapped at -196° without pumping.

The following mixture was identified:

CO_2, HCl: (identified by infrared spectrum[119,131]; confirmed by mass spectrum[4,1]; 4.95 mmole gas which corresponds to; HCl, 144. mg., 3.96 mmole; CO_2, 43.6 mg., 0.99 mmole; a 99% yield based on the initial CCl_4).

2. Reaction of Carbon Tetrachloride and Water at 800 Atmospheres.

Summary: The reaction of CCl_4 and H_2O at 800 atmospheres and 300° was found to occur readily within 12 hours as given by the equation,

$$CCl_4 + 2\ H_2O \rightarrow CO_2 + 4\ HCl \qquad (86)$$

Carbon tetrachloride (169 mg., 1.1 mmole) was transferred into

a gold tube containing H_2O (119 mg., 6.7 mmole). The tube was evacuated, sealed and held at 800 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material trapped at -196° without pumping.

The following material was identified:

CO_2, HCl: (identified by infrared spectrum[119,131]; confirmed by mass spectrum[4,1], HCl, 156.7 mg., 4.30 mmole; CO_2, 47.1 mg., 1.07 mmole; a 97% yield based on the initial CCl_4).

3. The Attempted Reaction of Carbon Tetrachloride and Water at 10 Atmospheres.

Summary: The reaction of CCl_4 and H_2O at 10 atmospheres and 300° did not occur within 12 hours,

$$CCl_4 + 2\ H_2O \rightarrow \text{No Reaction} \qquad (87)$$

Carbon tetrachloride (154 mg., 1.0 mmole) was transferred into a 25 ml glass ampule containing H_2O (119 mg., 6.7 mmole). The ampule was evacuated, sealed and heated at 300° for 12 hours, generating approximately 10 atmospheres of pressure.

The glass ampule was opened and the contents trapped at -196° in vacuo.

The following material was identified:

CCl_4, H_2O: (identified by infrared spectrum[173,130]; confirmed by mass spectrum[3,147].

4. The High Pressure Reaction of Trichlorofluoromethane and Water.

Summary: The reaction of $CFCl_3$ and H_2O was found to occur readily

at 4000 atmospheres and at 300° within 12 hours according to the following equation,

$$2\ CFCl_3 + 2\ H_2O \rightarrow CF_2Cl_2 + CO_2 + 4\ HCl \qquad (88)$$

$$3\ CF_2Cl_2 + 2\ H_2O \rightarrow 2\ CF_3Cl + CO_2 + 4\ HCl \qquad (89)$$

Trichlorofluoromethane (252.2 mg., 1.836 mmole) was condensed into a gold tube containing H_2O (59.4 mg., 3.33 mmole). The tube was sealed and held at 4000 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material trapped at -196° without pumping.

The following mixture was identified:

$CFCl_3$, CF_2Cl_2, CF_3Cl, CO_2 and HCl: (each species was identified by infrared spectrum[69,118,160,119,131]; confirmed by mass spectrum[5,6,149,4,1]; yield 2.51 mmole gas which corresponds to; $CFCl_3$, 207. mg., 1.51 mmole; CO_2, 7.4 mg., 0.17 mmole; HCl, 24.3 mg., 0.668 mmole; CF_2Cl_2, 20.2 mg., 0.17 mmole; CF_3Cl, 4.2 mg., 0.04 mmole; a 17.9% yield based on the initial amount of $CFCl_3$).

5. The Reaction of Trichlorofluoromethane and Water at 800 Atmospheres.

Summary: The reaction of $CFCl_3$ and H_2O was found to occur readily at 800 atmospheres and at 300° within 12 hours according to the equation,

$$2\ CFCl_3 + 2\ H_2O \rightarrow CF_2Cl_2 + CO_2 + 4\ HCl \qquad (90)$$

$$3\ CF_2Cl_2 + 2\ H_2O \rightarrow 2\ CF_3Cl + CO_2 + 4\ HCl \qquad (91)$$

Trichlorofluoromethane (119.7 mg., 0.872 mmole) was condensed into a gold tube containing H_2O (59.4 mg., 3.33 mmole). The tube was

sealed and held at 800 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material trapped at -196° without pumping.

The following mixture was identified:

$CFCl_3$, CF_2Cl_2, CF_3Cl, CO_2, HCl: (identified by infrared spectrum[69,118, 160,119,131]; confirmed by mass spectrum[5,6,149,4,1]; yield 1.19 mmole gas which corresponds to; $CFCl_3$, 98.1 mg., 0.714 mmole; CO_2, 3.47 mg., 0.079 mmole; HCl, 11.5 mg., 0.316 mmole; CF_2Cl_2, 9.55 mg., 0.079 mmole; CF_3Cl, 2.1 mg., 0.02 mmole; a 17.2% yield based on the initial amount of $CFCl_3$).

6. The Reaction of Trichlorofluoromethane and Water at 200 Atmospheres.

Summary: The reaction of $CFCl_3$ and H_2O at 200 atmospheres and 300° was found to occur readily within 12 hours as given by the following equation,

$$2\ CFCl_3 + 2\ H_2O \rightarrow CF_2Cl_2 + 4\ HCl + CO_2 \qquad (92)$$

$$3\ CF_2Cl_2 + 2\ H_2O \rightarrow 2\ CF_3Cl + 4\ HCl + CO_2 \qquad (93)$$

Trichlorofluoromethane (129.4 mg., 0.942 mmole) was condensed into a gold tube containing H_2O (59.4 mg., 3.33 mmole). The tube was sealed and held at 200 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material trapped at -196°.

The following mixture was identified:

$CFCl_3$, CF_2Cl_2, CF_3Cl, CO_2, HCl: (identified by infrared spectrum[69,118, 160,119, 131]; confirmed by mass spectrum[5,6,149,4,1]; yield 1.28 mmole gas which corresponds to; $CFCl_3$, 105. mg., 0.768 mmole; CO_2, 3.74 mg.,

0.085 mmole; HCl, 2.4 mg., 0.341 mmole; CF_2Cl_2, 10.3 mg., 0.085 mmole; CF_3Cl, 2.1 mg., 0.02 mmole; a 18.6% yield based on the initial amount of $CFCl_3$).

7. The Reaction of Trichlorofluoromethane and Water at 150 Atmospheres.

Summary: The reaction of $CFCl_3$ and H_2O at 150 atmospheres and 300° was found to occur within 12 hours as given by the following equation,

$$2\ CFCl_3 + 2\ H_2O \rightarrow CF_2Cl_2 + CO_2 + 4\ HCl \qquad (94)$$

Trichlorofluoromethane (104 mg., 0.761 mmole) was condensed into a 1 ml glass ampule containing H_2O (59.4 mg., 3.33 mmole). The ampule was sealed and heated at 300° for 12 hours, generating approximately 150 atmospheres of pressure.

The glass ampule was opened and the contents trapped at -196° in vacuo.

The following material was identified:

$CFCl_3$, CF_2Cl_2, HCl, CO_2: (identified by infrared spectrum[69,118,131,119]; confirmed by mass spectrum[5,6,1,4]; yield 0.838 mmole of gas which corresponds to; $CFCl_3$, 99.3 mg., 0.723 mmole; CO_2, 0.83 mg., 0.019 mmole; HCl, 2.8 mg., 0.077 mmole; CF_2Cl_2, 2.3 mg., 0.019; a 5% yield based on the initial amount of $CFCl_3$).

8. The Attempted Reaction of Trichlorofluoromethane and Water at 10 Atmospheres.

Summary: The reaction of $CFCl_3$ and H_2O did not occur within 12 hours,

$$CFCl_3 + H_2O \rightarrow \text{No Reaction} \qquad (95)$$

Trichlorofluoromethane (157.9 mg., 1.15 mmole) was condensed into a 25 ml glass ampule containing H_2O (59.4 mg., 3.33 mmole). The ampule was evacuated, sealed and heated at 300° for 12 hours, generating approximately 10 atmospheres of pressure.

The glass ampule was opened and the contents trapped at -196° in vacuo.

The following material was identified:

$\underline{CFCl_3, H_2O}$: (identified by infrared spectrum[69,130]; confirmed by mass spectrum[5,147]; $CFCl_3$, 147.0 mg., 1.07 mmole; a 94% yield based on the initial amount of $CFCl_3$).

9. The High Pressure Rearrangement of Trichlorofluoromethane.

Summary: The rearrangement of $CFCl_3$ at 4000 atmospheres and 300° was found to occur readily within 12 hours to yield the following products,

$$2\ CFCl_3 \rightarrow CF_2Cl_2 + CCl_4 \qquad (96)$$

Trichlorofluoromethane (166. mg., 1.21 mmole) was condensed into a gold tube, the tube was sealed and held at 4000 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material trapped at -196° without pumping.

The following mixture was identified:

$\underline{CFCl_3, CF_2Cl_2, CCl_4}$: (identified by infrared spectrum[69,118,173]; confirmed by mass spectrum[5,6,3]; 97.5% recovery of all gases; yields

determined on the basis of gaseous products, CF_2Cl_2 and $CFCl_3$; $CFCl_3$, 79.7 mg., 0.58 mmole; CF_2Cl_2, 36.3 mg., 0.30 mole; CCl_4, 46.1 mg., 0.30 mmole)

10. The High Pressure Reaction of Dichlorodifluoromethane and Water.

Summary: The reaction of CF_2Cl_2 and H_2O was found to occur readily at 4000 atmospheres and at 300° within 12 hours according to the following equation,

$$3\ CF_2Cl_2 + 2\ H_2O \rightarrow 2\ CF_3Cl + CO_2 + 4\ HCl \qquad (97)$$

Dichlorodifluoromethane (103.4 mg., 0.853 mmole) was condensed into a gold tube containing H_2O (59.4 mg., 3.33 mmole). The tube was sealed and held at 4000 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material trapped at -196° without pumping.

The following mixture was identified:

CF_2Cl_2, CF_3Cl, CO_2 and HCl: (each species was identified by infrared spectrum[118,160,119,131]; confirmed by mass spectrum[6,149,4,1]; yield 1.67 mmole gas which corresponds to; CF_2Cl_2, 27.1 mg., 0.224 mmole; CO_2, 8.94 mg., 0.203 mmole; HCl, 29.6 mg., 0.812 mmole; CF_3Cl, 42.4 mg., 0.406 mmole; a 74.0% yield based on the initial amount of CF_2Cl_2).

11. The Reaction of Dichlorodifluoromethane and Water at 800 Atmospheres.

Summary: The reaction of CF_2Cl_2 and H_2O was found to occur readily at 800 atmospheres and at 300° within 12 hours to yield the following products,

$$3\ CF_2Cl_2 + 2\ H_2O \rightarrow 2\ CF_3Cl + 4\ HCl + CO_2 \qquad (98)$$

Dichlorodifluoromethane (114 mg., 0.943 mmole) was condensed into a gold tube containing H_2O (59.4 mg., 3.33 mmole). The tube was sealed and held at 800 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material trapped at -196° without pumping.

The following mixture was identified:

CF_2Cl_2, CF_3Cl, HCl, CO_2: (identified by infrared spectrum[118,160,131,119]; confirmed by mass spectrum[6,149,1,4]; yield 2.10 mmole gas which corresponds to; CF_2Cl_2, 20.4 mg., 0.243 mg., 0.243 mmole; CO_2, 9.73 mg., 0.221 mmole; HCl, 32.2 mg., 0.883 mmole; CF_3Cl, 45.9 mg., 0.440 mmole; a 73.4% yield based on the initial amount of CF_2Cl_2).

12. The Reaction of Dichlorodifluoromethane and Water at 200 Atmospheres.

Summary: The reaction of CF_2Cl_2 and H_2O at 200 atmospheres and at 300° was found to occur readily within 12 hours as given by the equation,

$$3\ CF_2Cl_2 + 2\ H_2O \rightarrow 2\ CF_3Cl + 4\ HCl + CO_2 \qquad (99)$$

Dichlorodifluoromethane (111.9 mg., 0.926 mmole) was condensed into a gold tube containing H_2O (59.4 mg., 3.33 mmole). The tube was sealed and held at 200 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material trapped at -196° without pumping.

The following mixture was identified:

$\underline{CF_2Cl_2, CF_3Cl, CO_2, HCl}$: (identified by infrared spectrum[118,160,119,131]; confirmed by mass spectrum[6,149,4,1]; yield 1.81 mmole gas which corresponds to; CF_2Cl_2, 29.4 mg., 0.243 mmole; CO_2, 9.73 mg., 0.221 mmole; HCl, 32.2 mg., 0.883 mmole; CF_3Cl, 45.9 mg., 0.440 mmole; a 73.8% yield based on the initial amount of CF_2Cl_2).

13. The Reaction of Dichlorodifluoromethane and Water at 150 Atmospheres.

Summary: The reaction of CF_2Cl_2 and H_2O at 150 atmospheres and 300° was found to occur within 12 hours as given by the following equation,

$$3\ CF_2Cl_2 + 2\ H_2O \rightarrow 2\ CF_3Cl + CO_2 + 4\ HCl \qquad (100)$$

Dichlorodifluoromethane (118.7 mg., 0.982 mmole) was condensed into a 1 ml glass ampule containing (59.4 mg., 3.33 mmole). The ampule was sealed and heated at 300° for 12 hours, generating approximately 150 atmospheres of pressure.

The glass ampule was opened and the contents trapped at -196° in vacuo.

The following material was identified:

$\underline{CF_2Cl_2, CF_3Cl, CO_2, HCl}$: (identified by infrared spectrum[118,160,119,131]; confirmed by mass spectrum[6,149,4,1]; yield 1.02 mmole gas which corresponds to; CF_2Cl_2, 115. mg., 0.952 mmole; CO_2, 0.44 mg., 0.010 mmole; HCl, 1.46 mg., 0.040 mmole; CF_3Cl, 2.09 mg., 0.02 mmole; a 3% yield based on the initial amount of CF_2Cl_2).

14. The Attempted Reaction of Dichlorodifluoromethane and Water at 10 Atmospheres.

Summary: The reaction of CF_2Cl_2 and H_2O did not occur within 12 hours,

$$CF_2Cl_2 + H_2O \rightarrow \text{No Reaction} \qquad (101)$$

Dichlorodifluoromethane (137.8 mg., 1.14 mmole) was condensed into a 25 ml glass ampule containing H_2O (59.4 mg., 3.33 mmole). The ampule was evacuated, sealed and heated at 300° for 12 hours, generating approximately 10 atmospheres of pressure.

The glass ampule was opened and the contents trapped at -196° in vacuo.

The following material was identified:

CF_2Cl_2, H_2O: (identified by infrared spectrum[118,130]; confirmed by mass spectrum[6,119]; yield 139.0 mg., 1.15 mmole CF_2Cl_2; 100% recovery).

15. The Attempted High Pressure Rearrangement of Dichlorodifluoromethane.

Summary: The rearrangement of CF_2Cl_2 at 4000 atmospheres and 300° was found to occur within 12 hours,

$$2\ CF_2Cl_2 \rightarrow CF_3Cl + CFCl_3 \qquad (102)$$

Dichlorodifluoromethane (156 mg., 1.29 mmole) was condensed into a gold tube, the tube was sealed and held at 4000 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material trapped at -196° without pumping.

The following product was identified:

$\underline{CF_2Cl_2}$: (156 mg., 1.29 mmole; identified by infrared spectrum[118]; confirmed by mass spectrum[6]; 100% recovery of volatiles; very small but perceptible CF_3^+ and CCl_3^+ peaks appeared at m/e of 69 and 117, 119, 121 (3 Cl isotopic pattern) indicate some slight rearrangement (3-5 percent) which could not be picked up in infrared mixture.

16. The Attempted Reaction of Chlorotrifluoromethane and Water at 4000 Atmospheres.

Summary: The reaction of $CFCl_3$ and H_2O did not occur at 4000 atmospheres and at 300° according to the equation,

$$CF_3Cl + H_2O \rightarrow \text{No Reaction} \qquad (103)$$

Chlorotrifluoromethane (177.7 mg., 1.294 mmole) was condensed into a gold tube containing H_2O (59.4 mg., 3.33 mmole). The tube was sealed and held at 4000 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material trapped at -196° without pumping.

The following material was identified:

$\underline{CF_3Cl}$: (identified by infrared spectrum[160]; confirmed by mass spectrum[149]; yield 1.27 mmole, 174.4 mg., CF_3Cl; 98.5% recovery).

17. The Attempted Reaction of Tetrafluoromethane and Water at 4000 Atmospheres.

Summary: The reaction of CF_4 and H_2O did not occur at 4000 atmospheres and at 300° according to the equation,

$$CF_4 + H_2O \rightarrow \text{No Reaction} \qquad (104)$$

Tetrafluoromethane (72.8 mg., 0.827 mmole) was condensed into a gold tube containing H_2O (59.4 mg., 3.33 mmole). The tube was sealed and held at 4000 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material trapped at -196° without pumping.

The following material was identified:

CF_4: (identified by infrared spectrum[55]; confirmed by mass spectrum[2]; yield 0.818 mmole, 72.0 mg., CF_4; 99% recovery).

18. The Reaction of Dichlorodifluoromethane and Water at 800 Atmospheres.

Summary: The reaction of CF_2Cl_2 and H_2O was found to occur readily at 800 atmospheres and at 300° within 12 hours to yield the following products,

$$CF_2Cl_2 + H_2O \rightarrow CCl_4 + CFCl_3 + CF_3Cl + HCl + CO_2 + Cl_2Co \qquad (105)$$

Dichlorofluoromethane (114 mg., 0.943 mmole) was condensed into a gold tube containing H_2O (36. mg., 2 mmole). The tube was sealed and held at 800 atmospheres and 300° for 12 hours.

The gold tube was opened and the volatile material trapped at -196° without pumping.

The following mixture was identified:

CF_2Cl_2, CF_3Cl, $CFCl_3$, CCl_4, HCl, CO_2, Cl_2CO: identified by infrared spectrum[118,160,69,173,131,119,117]; confirmed by mass spectrum[6,149,5,3,1,4,117]; yield 2.10 mmole gas out; the products were too complicated (in number) to legitimately calculate yields.

TABLE V

Summary of $CCl_xF_{(4-x)}$ Hydrolysis

#	$CCl_xF_{(4-x)}$[a]	H_2O[a]	Press[b] Temp[c]	CO_2/HCl	PRODUCTS[a] CF_2Cl_2	CF_3Cl	$CFCl_3$	Other
1	CCl_4(1.00)	6.6	4000	0.99/3.96	-----	-----	-----	
2	CCl_4(1.10)	6.6	800	1.07/4.30	-----	-----	-----	
3	CCl_4(1.0)	6.6	10	----	-----	-----	-----	1.0[d]
4	$CFCl_3$(1.84)	6.6	4000	0.167/0.688	0.167	0.04	1.51	
5	$CFCl_3$(0.872)	6.6	800	0.079/0.316	0.079	0.02	0.714	
6	$CFCl_3$(0.942)	6.6	200	0.085/0.341	0.085	0.341	0.768	
7	$CFCl_3$(0.761)	6.6	150	0.019/0.077	0.019	-----	0.723	
8	$CFCl_3$(1.15)	6.6	10	----	-----	-----	1.07	
9	$CFCl_3$(1.21)	---	4000	----	0.30	-----	0.58	0.30[d]
10	CF_2Cl_2(0.853)	6.6	4000	0.203/0.812	0.224	0.406	-----	
11	CF_2Cl_2(0.943)	6.6	800	0.224/0.898	0.246	0.447	-----	
12	CF_2Cl_2(0.936)	6.6	200	0.221/0.883	0.243	0.440	-----	
13	CF_2Cl_2(0.982)	6.6	150	0.010/0.040	0.952	0.02	-----	
14	CF_2Cl_2(1.14)	6.6	10	----	1.15	-----	-----	
15	CF_2Cl_2(1.29)	---	4000	----	1.23	0.03	0.03	
16	CF_3Cl (1.29)	6.6	4000	----	-----	1.28	-----	
17	CF_4(0.827)	6.6	4000	----	-----	-----	-----	0.828[e]
18	CF_2Cl_2(0.943)	2.0	800	Mixture: $HCl, CO_2, CCl_4, CFCl_3, CF_2Cl_2, CF_3Cl, Cl_2CO$				

[a] The quantities are given in millimoles.

[b] Pressure is given in atmospheres

[c] All reactions were carried out at 300°.

[d] Carbon Tetrachloride

[e] Carbon Tetrafluoride

I. The Reaction of $Cl_3SiCo(CO)_4$ and PF_3 at an Ideal Gas Pressure of 40 Atmospheres.

Summary: In a preliminary experiment it was found that a series of PF_3 substituted compounds could be obtained by the reaction of PF_3 with $Cl_3SiCo(CO)_4$ at 40 atmospheres and 50° with ultraviolet irradiation for 12 hours according to the following equation,

$$Cl_3Si\text{-}Co(CO)_4 + nPF_3 \rightarrow [Cl_3Si\text{-}Co(CO)_x(PF_3)_{(3-x)}]_z \qquad (106)$$

---

a. Synthesis:

Phosphorus trifluoride (3.352 g., 38.1 mmole) was condensed into a 25 ml glass pressure reactor with a Teflon stopcock containing $Cl_3SiCo(CO)_4$ (1.2258 g., 4.014 mmole). The stopcock was closed and the pressure vessel allowed to warm to room temperature with the manometer used to check for a leak from the pressure vessel.

After checking for leaks, a water jacket (RT) was placed around the pressure vessel and the uv light source (GE PAR 38 SPOT, code H100PSP44-4, ASA-H44-4GS) and shielding positioned.

The uv lamp was cut on and the cooling water flow rate adjusted so as to limit the maximum temperature to 50° so that the $Cl_3SiCo(CO)_4$ would be liquid (m.p. 44.5° - 45.0°).

After two hours, the uv source was turned off and the pressure vessel allowed to cool to room temperature. It was then cooled to -196°, with the liquid nitrogen level rising to the teflon-glass stopcock seal, allowing leakage past the seal. All non-condensibles were then removed with pumping (assumed to be displaced CO which has 400 torr pressure at -196°).

The photolysis was repeated several times until little or no non-condensible materials were observed on the manometer and thus most of the CO had been displaced. This requires 12 to 15 hours of photolysis.

A color change and physical change are observed almost immediately upon initial photolysis and heating, the amber crystals turn into an oily viscous red liquid, typical of some Co complexes.

Some dark brown decomposition product is also observed in the reaction vessel. This is believed to be a thermal decomposition product as copious quantities of $SiCl_4$ were distilled out of the reaction mixture at -35°. Silicon tetrafluoride is known to be a thermal decomposition product of $F_3SiCo(CO)_4$[60].

After reaction, the mixture can be stored in the reaction vessel for several weeks at room temperature with only slight decomposition.

b. Identification:

$[(Cl_3Si)\text{-}Co\text{-}(CO)_x(PF)_{3-x}]_z$ was first identified by infrared spectrum. A gas phase infrared spectrum clearly shows the presence of coordinated CO(2040 cm^{-1}, 2075 cm^{-1} and 2110 cm^{-1}), coordinated PF_3(857 cm^{-1}, 890 cm^{-1}, 910 cm^{-1}) and $SiCl_3$(610 cm^{-1}). It was obvious from the infrared spectrum that some PF_3 had displaced some of the CO in the starting material.

The fluorine 19 magnetic resonance spectrum of the product consisted of several doublets and triplets not well defined with at least 3 different environments where J_{PF} was in the range of 1320 Hz to 1350 Hz and an extraneous peak upfield where J_{PF} would have a value of 1400 Hz. Coordinated PF_3 norma-ly has a J_{PF} in the 1300 Hz to 1350 Hz range while PF_3 has a J_{PF} of ∿1400 Hz. In general the F-NMR indicates that

a PF_3 coordination compound is present but a more detailed study would be needed to interpret the complex spectra of an obviously complex mixture.

The mass spectrum of the reaction mixture initially indicated the presence of $Cl_3SiCo(CO)_x(PF_3)_{3-x}$ and copious quantities of $SiCl_4$. The $SiCl_4$ is an expected decomposition product and the absence of parent ions in the $Cl_3SiCo(CO)_x(PF_3)_{4-x}$ series is not unexpected because many coordination complexes do not exhibit a parent ion peak. It should be noted that authentic samples of $Cl_3SiCo(CO)_4$[12] exhibit a very weak parent ion (∿1% total ion current) with the operating parameters used in this study.

After cooling the mass spectrometer to room temperature, another series of spectra were taken in an attempt to observe the parent ion $Cl_3SiCo(PF_3)_4$ at m/e 545.

The parent ion at m/e 545 did not appear but instead a series of weak peaks having a six Cl isotopic pattern (m, 50%; M+2, 100%; m+4, 83%; m+6, 37%; m+8, 9.25%; m+10, 1.2%) were observed. The very high mass number (m/e) and isotopic pattern suggest a dimeric species. The low intensity of these high mass number peaks coupled with the fact that they disappear when the ion source on the mass spectrometer reaches ∿50° suggest that the dimer bond (Co-Co) is quite weak.

Accurate calibration of mass spectra obtained with an instrument that does not have a linear sweep requires calibration standards.

The data in Table VI has been obtained using perfluorokerosene (PFK) as an internal standard. Above m/e = 750 the masses were assigned using extrapolations and are valid to only about ± 5 mass numbers.

Table VI lists the m/e observed up to mass 825 with the specie postulated. It is significant to note that these m/e ratios do not include six coordinating ligands around the two Co atoms, but only five. This does not discount the presence of the sixth ligand, only the stability of that species in the mass spectrum as a cation.

TABLE VI

Mass Spectral Data

$[Cl_3SiCo(CO)_x(PF_3)_{3-x}]_2$ [b]

m/e	I	I/I_o	% T.I.C.[a]	Species[c]
824	0.2	1.8	0.19	$R_2(PF_3)_5^+$
784	0.4	3.3	0.35	$R_2(PF_3)_4(CO)^+$
704	0.4	3.3	0.35	$R_2(PF_3)_2(CO)_3^+$
644	0.4	3.3	0.35	$R_2(PF_3)_2(CO)_3^+$
584	0.4	3.3	0.35	$R_2(PF_3)_1(CO)_4^+$
524	0.3	2.7	0.28	$R_2(CO)_5^+$
456	1.0	8.3	0.85	$R\text{-}(PF_3)_3^+$
395	1.65	3.7	1.41	$R\text{-}(PF_3)_2(CO)^+$
368	2.8	23.3	2.38	$R\text{-}(PF_3)_2^+$
349	0.6	5.0	0.5	$R\text{-}(PF_3)_1PF_2^+$
336	1.8	15.0	1.5	$R\text{-}(PF_3)(CO)_2^+$
308	3.2	27.0	2.8	$R\text{-}(PF_3)(CO)^+$
289	0.8	6.7	0.7	$R\text{-}(CO)PF_2^+$
280	2.1	17.0	1.7	$R\text{-}(PF_3)^+$
248	3.3	27.0	2.7	$R\text{-}(CO)_2^+$
220	9.9	82.0	8.4	$R\text{-}(CO)^+$
192	9.2	77.0	7.9	$CoSiCl_3^+$
175	3.6	30.0	3.1	$Co(CO)(PF_3)$
157	4.4	37.0	3.8	$CoSiCl_2^+$
147	12.0	100.0	10.2	$Co(PF_3)^+$

$[Cl_3SiCo(CO)_x(PF_3)_{3-x}]_2$ - continued

m/e	I	I/I_o	% T.I.C.[a]	Species
122	2.0	16.7	1.7	$CoSiCl^+$
94	1.9	16.0	1.6	$CoCl^+$
88	13.8	115	11.8	PF_3^+
87	5.8	48.0	4.9	$CoSi$, $CoCO^+$
69	17.1	142	14.5	PF_2^+
63	7.9	66.0	6.7	$SiCl^+$
59	10.8	90.0	9.2	Co^+
50	1.0	8.0	0.8	PF^+
31	0.7	6.0	0.6	P^+

[a] T.I.C. = total ion current.

[b] Monoisotopic mass spectrum for $^{35}_{17}Cl$.

[c] R = Cl_3Si-Co.

CHAPTER III

DISCUSSION

A. Interaction of Phosphorus Trifluoride with Transition Metal Oxides.

This research was undertaken in an attempt to study the reducing properties of PF_3 at high pressure and elevated temperature. The two stable oxidation states of P(III and V) coupled with the ability of PF_3 to act as a Lewis base (σ-bonded) and Lewis acid (π-acceptor) simultaneously implies that under the appropriate conditions PF_3 may react with transition metal oxides according to the equation

$$MO_x + (x+y)PF_3 \rightarrow M(PF_3)_y + xOPF_3 \qquad (107)$$

This reaction is analogous to that described in the introduction as the "reductive fluorophosphination" of transition metal salts[70].

1. Summary. As indicated in Table IIIB, the reaction of NiO with PF_3 at 4000 atmospheres and 300° proceeded as proposed, $Ni(PF_3)_4$ and OPF_3 being formed. This was the only reaction to proceed directly from the reaction of PF_3 and the transition metal oxide.

In the reductive fluorophosphination of the transition metal halides, Hieber[70] had used a Group IB metal Cu or a Group IIB metal Zn to reduce the metal halide to form $CuCl_2$ or $ZnCl_2$. Because of the increased stability of the transition metal oxides compared to chlorides,

it was decided to use Mg (Standard Reduction Potential -2.37v.) rather than Cu(S.R.P. + 0.15 v.) or Zn(S.R.P. - 0.76 v.) as an added reducing agent.

In the presence of Mg, NiO, MoO_3 and WO_3 were observed to react with PF_3 at 4000 atmospheres and 300° by reductive fluorophination, according to the equation,

$$\underset{(m=Mo,W)}{MO_3} + 9\ PF_3 \xrightarrow{Mg} M(PF_3)_6 + 3\ OPF_3 \qquad (108)$$

As indicated in the next section, OPF_3 underwent further reaction with the Mg to yield $P_2O_3F_4$.

However, if the reaction was carried out with magnesium at 100 atmospheres and 300° with NiO, MoO_3 and WO_3, only NiO reacts forming $Ni(PF_3)_4$ and OPF_3. No reaction to any extent was observed with MoO_3 or WO_3.

As indicated in Table IIIA, CrO_3 and Cr_2O_3 were combined several times with PF_3 and Mg at 4000 atmospheres and 300° in an attempt to synthesize $Cr(PF_3)_6$. No $Cr(PF_3)_6$ was isolated although significant amounts of OPF_3 were observed indicating the Cr_2O_3 and CrO_3 had been partially reduced.

Numerous other transition metal oxides were combined with PF_3 and Mg at 4000 atmospheres and 300°. Table IIIB lists these oxides and the products of their reactions which include PF_3, OPF_3 and $P_2O_3F_4$ or its hydrolysis products.

2. Influence of Pressure. The significance of pressure in the reductive fluorophosphination of transition metal oxides can best be interpreted in light of the fluorophosphination reaction. The

introduction cites the use of PF_3 to reduce SO_2, SeO_2 and TeO_2[31] in a flow system at high temperature (300° - 600°) and low pressure indicating that the reducing properties of PF_3 towards oxides are primarily a function of temperature. The increase in pressure should certainly increase the rate of the reduction due to the large increase in concentration of the reactants.

The fluorophosphination of the reduced metal is known to be pressure dependent. Nickel, Palladium and platinum are known to react directly with PF_3 at 100-200 atmospheres[83] with the metal being generated by thermal decomposition of the oxalate, viz.

$$M(C_2O_4) \rightarrow M + 2\ CO_2 \qquad (109)$$

$$M + 4\ PF_3 \rightarrow M(PF_3)_4 \quad (m=Ni,Pd \text{ or } Pt) \qquad (110)$$

The reaction of the metal with PF_3 results in a net loss of gaseous reactant and is thus theoretically pressure favored.

3. Bonding in Transition Metal-Phosphorus Trifluoride Complexes. The transition metal PF_3 complexes are similar to the corresponding carbonyl compounds in structure and physical properties. A major difference in the two classes of compounds is the inability of PF_3 to form bridge bonds between the transition metals[36] as commonly observed with CO. The bonding of the transition metal and PF_3 can be represented by the following scheme,

$$M \rightleftharpoons PF_3$$

It should be noted that the double arrow of the M-PF_3 bond is only a symbol for the bonding and does not denote a true (p-p)π double bond. It does represent a σ-bond formed by the contribution of a lone pair of electrons from phosphorus to the metal (p-d)σ and a back donation of a

non-bonded pair of electrons from the metal to phosphorus (d-d)π.

4. Discussion. This research has shown that PF_3 can be used in the reduction and fluorophosphination of transition metal oxides in the presence of magnesium. It is not unexpected that PF_3 will reduce transition metal oxides at high pressure and elevated temperature. This reduction was observed in all of the reactions attempted with the formation OPF_3 and $P_2O_3F_4$.

The formation of $Ni(PF_3)_4$ after the reduction of the NiO to Ni supports previous experimental results of nickel-PF_3 syntheses. The most unusual result of this research is the reduction of WO_3 and MoO_3 in the presence of Mg with PF_3 to yield $Mo(PF_3)_6$ and $W(PF_3)_6$. Since the reaction doesn't occur without the Mg, the Mg may be included in a proposed reaction pathway, viz.

$$MO_3 + 3\ Mg \rightarrow M + 3\ MgO \qquad (111)$$

$$M + 6\ PF_3 \rightarrow M(PF_3)_6 \text{ (where M=Mo,W)} \qquad (112)$$

This proposed reaction pathway adds W and Mo to the list of transition metals (Ni,Pd,Pt)[83] that will react directly with PF_3 to form the corresponding coordination compound.

The next section will discuss the side reactions observed when Mg is present in a system containing P-O-F compounds.

B. Interaction of Phosphorus Trifluoride with Group VIA Elements.

This research was undertaken to study the reducing properties of PF_3 on the elements O_2, S, Se and Te. It has long been known[178] that PF_3 reacts readily at low temperature and atmospheric pressure with the Group VIIA elements, the halogens, to form the corresponding tri-

fluorophosphorus (V) dihalide, viz.

$$PF_3 + X_2 \rightarrow PF_3X_2 \ (X=F, Cl, Br) \tag{113}$$

with PF_3Br_2 disproportionating, viz. 124

$$5\ PF_3Br_2 \rightarrow 3\ PF_5 + 2\ PBr_5 \tag{114}$$

However, PF_3 reacts with O_2 at room temperature and atmospheric pressure only when initiated by a silent electrical discharge[171], viz.

$$PF_3 + O_2 \rightarrow OPF_3 + P_2O_3F_4 + (PO_2F)_n \tag{115}$$

Very little OPF_3 is formed in this reaction, with higher molecular weight species predominating. Corresponding reactions with S and Se have not been reported.

1. Summary. It was observed that PF_3 did not react with O_2, S or Se at 300° and one atmosphere pressure for 4 hours.

As indicated in Table IV, O_2 and PF_3 did not react at 4000 atmospheres and 25° for 12 hours. Tellurium was not observed to react with PF_3 at 4000 atmospheres for 12 hours at 300° or at 500°. The Te did alloy the gold tubing at 500°, viz.

$$Au + Te \rightarrow (Au\text{-}Te)\ alloy. \tag{116}$$

However, at 4000 atmospheres and 300° for 12 hours, O_2, S and Se were observed to react with PF_3, viz.

$$PF_3 + 1/2\ O_2 \rightarrow OPF_3 \tag{117}$$

$$PF_3 + S \rightarrow SPF_3 \tag{118}$$

$$PF_3 + Se \rightarrow SePF_3 \tag{119}$$

Sulfur was observed to react with PF_3 at 200 atmospheres and 300° with a 53% conversion but at 4000 atmospheres and 200° only 14% conversion to SPF_3 was achieved. At 500° and 4000 atmospheres Se reacted readily with PF_3 and with Au, viz.

$$Se + Au \rightarrow (Au\text{-}Se)\ alloy \qquad (120)$$

In an attempt to determine the source of a $P_2O_3F_4$ in the transition metal oxide - PF_3 reactions previously discussed where Mg was used as a reducing agent, O_2 and PF_3 were combined in the presence of Mg metal at 4000 atmospheres and 300°.

In the initial attempt, no $P_2O_3F_4$ was actually isolated, only the difluoro- and fluoro- phosphoric acids. These acids are products of the hydrolysis of $P_2O_3F_4$, viz.[20]

$$P_2O_3F_4 + H_2O \rightarrow 2\ HO_2PF_2 \qquad (121)$$

$$HO_2PF_2 + H_2O \rightarrow H_2O_3PF + HF \qquad (122)$$

The desired product, $P_2O_3F_4$, was isolated only after the gold tubing and opener were thoroughly dried with a CH_4/O_2 flame before use. The gold tubing was hard before heating to red heat but became quite malleable after heating. Vapors were observed diffusing out of the open end of the gold tube during heating.

After drying the tubing, the reaction proceeded, viz.

$$2\ O_2 + 3\ PF_3 + Mg \rightarrow OPF_3 + P_2O_3F_4 + MgF_2 \qquad (123)$$

The MgF_2 is proposed as this technique doesn't permit ready analysis of non-volatile solids. As no $P_2O_3F_4$ was observed in the reaction of O_2 and PF_3 without Mg, it is reasonable to propose that the Mg metal supplies a reaction route for the formation of $P_2O_3F_4$. To further clarify the role of the Mg, pure OPF_3 was combined with Mg under the same reaction conditions, yielding a small amount of $P_2O_3F_4$. The role of Mg was still uncertain because the reactive Mg metal would be expected to have an oxide coating which could serve as an intermediate, viz.

$$2\ OPF_3 + MgO \rightarrow P_2O_3F_4 + MgF_2 \qquad (124)$$

Next, an attempt was made to synthesize $P_2S_3F_4$ by the same reaction sequence without success, SPF_3 being the only product.

The synthesis of OPF_3 is most commonly achieved by the reaction of PF_5 with borosilicate glass (SiO_2) with catalytic amounts of H_2O, viz.[131],

$$2\ PF_5 + SiO_2 \rightarrow 2\ OPF_3 + SiF_4 \qquad (125)$$

This reaction is believed to proceed by the initial formation of HF and OPF_3,

$$PF_5 + H_2O \rightarrow 2\ HF + OPF_3 \qquad (126)$$

followed by the action of HF on SiO_2 to regenerate H_2O,

$$4\ HF + SiO_2 \rightarrow 2\ H_2O + SiF_4 \qquad (127)$$

In practice this method of synthesis is slow, requiring at least 12 hours to prepare a few millimoles of OPF_3. A further drawback is that the desired product (OPF_3) must be carefully vacuum distilled at low temperature.

It was found in this research that OPF_3 could be synthesized in good yield at one atmosphere and 300° by the reaction of O_2 and PF_5 in the presence of Mg metal. If the reaction was heated for 15 - 20 minutes, an 80% yield of OPF_3 was obtained with insignificant amounts of SiF_4 and a small amount of the lower volatile $P_2O_3F_4$ was also formed. If the reaction was heated for 2 - 3 hours, larger quantities of $P_2O_3F_4$ may be obtained along with larger quantities of SiF_4 and the silyl ether, $F_3SiOSiF_3$[113].

Further reactions were done at 1 atm and 300° to attempt to determine the role of the Mg. When PF_5 was reacted with MgO for 2 hours, some OPF_3 was formed (46% conversion). Also, in the reaction of OPF_3

and MgO under the same conditions, small amounts of $P_2O_3F_4$ were observed (14% conversion).

At low pressure the role of the Mg in the reactions of P-O-F systems can then be attributed to the oxide coating on the metal surface, rather than the metallic surface itself. If this is extended to the high pressure system, a reaction route can be formulated for the reaction of PF_3 and O_2 to yield $P_2O_3F_4$. Step one would be the formation of OPF_3, viz.

$$PF_3 + 1/2\ O_2 \rightarrow OPF_3 \qquad (128)$$

which has been shown to occur without the presence of Mg. Step two would then be the reaction of surface Mg/MgO with the OPF_3 in excess O_2, viz.

$$3\ OPF_3 + MgO \rightarrow P_2O_3F_4 + MgF_2 \qquad (129)$$

2. Influence of Pressure. This study has shown that pressure has a direct influence on the reduction of O_2, S and Se by PF_3 at 300°. It has also shown that the formation of $P_2O_3F_4$ is not pressure dependent in the presence of Mg/MgO.

As indicated in the introduction, a reaction containing gaseous reactants and products will generally be pressure favored if the volume of gaseous product will be less than gaseous reactant. This principle is applicable to the reaction of O_2 and PF_3,

$$2\ PF_3 + O_2 \rightarrow 2\ OPF_3 \qquad (130)$$

where 3 moles of reactant yield 2 moles of product.

In the reaction of S with PF_3, it is possible to have two different methods. The first would be the reaction of gaseous S at 300° with the PF_3 yielding SPF_3 with a resultant decrease in gaseous volume. The

second method would be the reaction of PF_3 with liquid S where the transition state would have a negative ΔV_o^* because the gas (PF_3) was momentarily part of a liquid species. The overall volume change would not decrease from reactants to products.

The reaction of Se with PF_3 presents the same pressure influences as the sulfur reaction. The vapor pressure of Se is only a few cm Hg at 300° but this does not prohibit the possibility of a gas phase reaction.

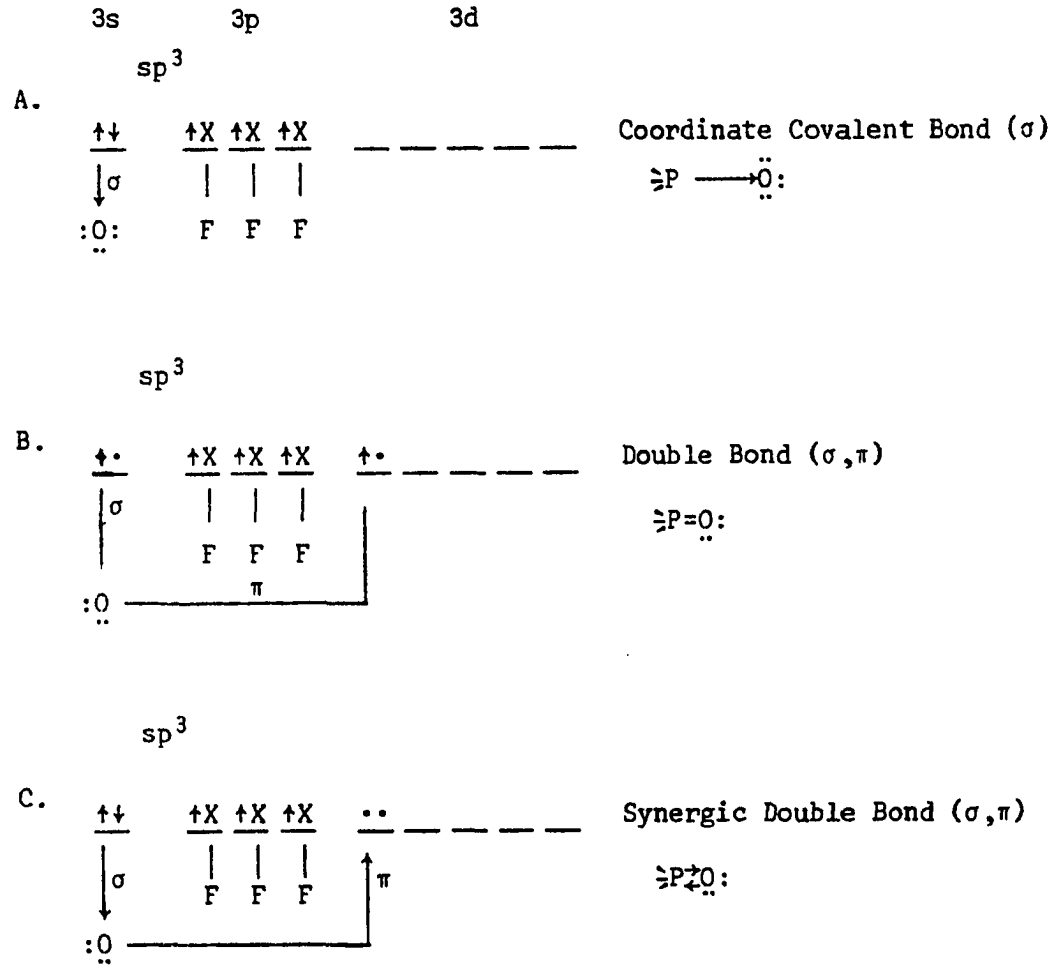
The Te has very little vapor pressure at all at 300° which may account for its non-reactivity towards PF_3.

3. Bonding in XPF_3. The valence bond approach to bonding permits at least three descriptions of the PO or PS linkage. The electronic configuration of the phosphorus atom is $1s^2 2s^2 2p^6 3s^2 3p^3$ which indicates that five electrons are available for bonding in the valence shell. In addition the empty d orbitals of P are close in energy to the 3p orbitals making them available to accept electron density from X(O,S or Se).

In Figure 5 the coordinate covalent, the double and the synergic (reciprocal coordinate covalent) bonding schemes are outlined.

Both OPF_3 and SPF_3 are believed to have significant double bond character. The novel compound $SePF_3$ should also have significant double bond character.

The OPF_3 is stable in air and hydrolyzes very slowly. On the other hand, SPF_3 burns in air but still hydrolyzes very slowly as indicated in the introduction with the P-F bonds being attacked yielding the thio-fluorophosphoric acids. This would indicate that combustion in



Bonding in OPF_3 (or SPF_3)

Figure 5

air involves the following reaction,

$$2\ SPF_3 + 3\ O_2 \rightarrow 2\ SO_2 + 2\ OPF_3 \qquad (129)$$

The compound, OPF_3, is thermally stable at 1 atm and 300°, but SPF_3 is reported to decompose under these conditions, viz.[186]

$$SPF_3 \rightarrow S + PF_3 \qquad (130)$$

Thus a trend is indicated where the XPF_3 derivatives become less thermally and chemically stable going down Group VIA in the periodic table.

This research extends this trend to the next element where X = Se. The compound $SePF_3$ was observed to have only fair stability decomposing slightly in the vacuum line and the infrared gas cell with deposition of a reddish solid believed to be Se. The nature of this decomposition is not understood at this time, but it is believed to be related to the photoelectronic character of Se,

$$SePF_3 \rightarrow Se + PF_3 \qquad (131)$$

This research has shown that high pressure can be used to synthesize some novel species by the direct reduction of a Group VI element by PF_3. It has also been shown that under conditions of high pressure and elevated temperature that the Group VIA elements react similar to the Group VIIA elements, the halogens.

A final result has been to show the use of Mg (or Mg/MgO) to synthesize OPF_3 and $P_2O_3F_4$ at low or high pressure. These reactions are new syntheses for these compounds.

C. Hydrolysis of Fluorochloromethanes.

As discussed in the introduction the fluorochloromethanes are

noted for their non-reactivity. This study was done in order to characterize the reactivity of this group of compounds towards water at high pressure and to identify the reaction intermediates where possible. It has also served as a study of the significance of pressure on the rate of hydrolysis.

1. Summary. As indicated in Table IV, it was observed that selected fluorochloromethanes do hydrolyze significantly above 200 atmospheres pressure at 300°, viz.

$$CF_xCl_{(4-x)} + 2\ H_2O \rightarrow CO_2 + 4\ HCl + n\ CF_3Cl \qquad (132)$$

(where x = 0,1,2)

CF_3Cl and CF_4 did not react at these conditions. In the reactions with a stoichiometric excess (4x) of water no lower fluorine content species than that of the reactant were observed but higher fluorine content species were observed where possible, i.e.

$$3\ CF_2Cl_2 + H_2O \rightarrow CO_2 + 4\ HCl + 2\ CF_3Cl \qquad (133)$$

No CF_4 was observed in the reactions that occurred with correlates with the observation that CF_3Cl doesn't hydrolyze.

Experimental results show that $CFCl_3$ rearranges at high pressure at 300°, viz.

$$2\ CFCl_3 \rightarrow CF_2Cl_2 + CCl_4 \qquad (134)$$

The degree of rearrangement was 53% after 12 hours. No experiments were run for longer periods of time to see if this were an equilibrium process.

Very minute rearrangement was observed with CF_2Cl_2 after 12 hours. Again, no equilibrium studies were done. The rearrangement was less than 5% as determined by mass spectral analysis, viz.

$$2\ CF_2Cl_2 \rightarrow CF_3Cl + CFCl_3 \qquad (135)$$

When the hydrolysis of CF_2Cl_2 was attempted with one third the normal water used, a series of different products was observed including HCl, CO_2, CCl_4, $CFCl_3$, CF_3Cl, and Cl_2CO.

The presence of CCl_4, $CFCl_3$ and Cl_2CO in this reaction with insufficient water infers that they are reaction intermediates. The mass spectrum of this reaction while quite complex, showed the presence of SiF_4 (me/ 85 with Si isotopic pattern) which indicates the existence of HF in the reaction mixture since HF reacts readily with borosilicate glass (SiO_2), viz[107].

$$4\ HF + SiO_2 \rightarrow SiF_4 + 2\ H_2O \qquad (136)$$

As indicated in the introduction, Cl_2CO is known to hydrolyze rapidly to CO_2 and HCl and is also known to be an intermediate in the hydrolysis of CCl_4 at 1 atmosphere in the gas phase above 350°[52].

The extent of hydrolysis varied with reactant. Using the same amount of H_2O in each instance, CCl_4 was hydrolyzed 100%, $CFCl_3$ was hydrolyzed 18% and CF_2Cl_2 was hydrolyzed 75%. The reason for this experimental observation is not fully understood. It would have been expected that $CFCl_3$ would hydrolyze to a greater extent than CF_2Cl_2 because of its higher chlorine content. This peculiarity will be explored further in the following sections.

2. Significance of High Pressure. As the hydrolysis of the fluorochloromethanes did not occur below 200 atmospheres to any significant degree in this isothermal study it is obvious that pressure is needed to initiate the reaction at 300°.

From the viewpoint of the novice, a reaction of this type would

not be expected to be pressure favored. For example, in the hydrolysis of CF_2Cl_2, viz.

$$3\ CF_2Cl_2 + 2\ H_2O \rightarrow CO_2 + 4\ HCl + 2\ CF_3Cl \qquad (137)$$

If all the reactants and products were considered to be gaseous (critical temperature of H_2O is 385°) representing the most limited pressure sensitive case, 5 moles of reactant will yield 7 moles of products. This is clearly not a pressure favored process. However, if the reaction is considered in light of the excess H_2O acting as a polar solvent, the compatability of the reaction at high pressure is better understood. As indicated in the introduction, the partial molal volume for CO_2 dissolving in H_2O to give H_2CO_3 is -27 cm^3/mole and for HCl about -15 cm^3/mole or greater. In view of these estimates of ΔV_o^* the partial molal volume of these two components should still be negative under the reaction conditions[89]. The reaction can now be considered to be the sum of two parts, viz.

$$2\ H_2O \rightarrow (4\ HCl + CO_2)\ \text{in}\ H_2O \qquad (138)$$

$$3\ CF_2Cl_2 \rightarrow 2\ CF_3Cl \qquad (139)$$

The negative ΔV_o^* for HCl and CO_2 make this reaction part very pressure favored while the second part indicates three moles of gas going to two moles of gas, which is also a pressure favored process. The net result is an overall reaction that is strongly pressure favored.

Similar arguments may be applied to the hydrolysis of CCl_4 and $CFCl_3$ with the conclusion that the reactants are also pressure favored. A summary of the reactions shows the observed products of hydrolysis,

$$CCl_4 + 2\ H_2O \rightarrow CO_2 + 4\ HCl \qquad (140)$$

$$2\ CFCl_3 + 2\ H_2O \rightarrow CO_2 + 4\ HCl + CF_2Cl_2 \qquad (141)$$

$$3\ CF_2Cl_3 + 2\ H_2O \rightarrow CO_2 + 4\ HCl + 2\ CF_3Cl \qquad (142)$$

The reaction of CCl_4 indicates that there is sufficient water (4X) to accommodate 100% of the stoichiometric amount of CO_2 and HCl possible. This leaves three possibilities for the greater reactivity of CF_2Cl_2 over $CFCl_3$. The first possibility is that the two reactions are rate controlled with CF_2Cl_2 reacting faster than $CFCl_3$. A second possibility is that the equilibrium constant in the CF_2Cl_2 reaction is larger than that of the $CFCl_3$ reaction. A final possibility is that $CFCl_3$ is hydrated more than CF_2Cl_2 under the reaction conditions and unable to react as readily coupled with removing solvating molecules from HCl and CO_2.

It seems that this preliminary research has indeed raised some questions about the ease of hydrolysis of fluorochloromethanes at high pressure. Hamilton[64] comments in his review of the organic fluorochemicals industry that "CF_2Cl_2 is significantly more stable to hydrolysis than $CFCl_3$" without citing a reference or indicating the reaction conditions. This research has shown that the hydrolysis is indeed pressure favored at 300°. Gaisinovich and Ketov[52] have shown that significant hydrolysis of CCl_4 begins at 350° (~5%/hour) at atmospheric pressure in the vapor phase. There is no reported data on the hydrolysis of CF_2Cl_2 or $CFCl_3$.

3. Mechanism of Hydrolysis. Mechanisms of fluorine displacement in organic systems have recently been reviewed by Parker[125] using the relative rates of displacement of Cl and F for comparative purposes. He concluded that because of the much greater bond strength and polarity in the fluoride (R-F) than in the chloride (R-Cl), the

reactivity difference seems to be usually large and unambiguous in direction, the fluoride either reacting very much more rapidly than the chloride, or very much more slowly.

The mechanism of halogen displacement from an organic halide RX by a nucleophile Y can be represented by the equation,

$$Y + R\text{-}X \rightarrow \overset{+}{Y} - R + X^{-} \qquad (143)$$

This may be followed by rapid proton transfer (i.e. if Y = H_2O) and it may be modified if the reagent is an anion, but the process will always be essentially the same, Y becoming one unit more positive, X becoming one unit more negative, and one bond being broken and one being formed.

The above reaction gives rise to three different possible mechanisms. The R-X bond can be broken before the Y-R is formed. This would represent a substitution-nucleophilic-1st Order (S_N1) reaction. The R-X bond can be broken just as the Y-R bond is being formed or the R-X bond can be broken after the Y-R bond is formed, both of which represent an S_N2 mechanism.

In considering the mechanism of halogen displacement at atmospheric pressure two major factors must be considered. One is the much stronger R-F bond over the R-Cl bond and the other factor is the ability of fluoride ions to form strong hydrogen bonds. As indicated in the introduction, le Noble[89] summarizes that at high pressure the data available indicate that the activation volume (ΔV_o^*) becomes more negative the smaller the halogen atom. In the study of reactions having ionic transition states, Perrin and Williams[126] have determined that the development of charges in the transition states invariably causes

pressure to increase the rate of reaction.

The mechanism of halogen displacement for the observed fluorochloromethane reactions can be predicted considering the solvent effect on charged transition states and the more negative activation volume of fluorine over chlorine.

The mechanistic routes can best be elucidated by comparing sets of reactions. For example, the hydrolysis of $(CF_3)Cl$ and $(CF_3)F$ does not occur. In other words, $Y(H_2O)$ does not displace Cl or F from CF_3 = R. As Cl^- and F^- are stable species in polar solvents at high pressure, this non-reactivity is indicative of the instability of the CF_3^+ moiety, viz.

$$CF_3X + H_2O \rightarrow [H_2O\cdots\cdots\overset{+}{C}F_3\cdots\cdots\cdots X^-] \qquad (144)$$

(charges in this transition state represent partial charges). This reaction does not proceed to any intermediate.

From the standpoint of stability of various fluorinated cations, CCl_3^+ and CF_3^+ may be used as the extreme comparisons. Due to the strong electronegativity of fluorine (4.0 on Pauling's scale) compared to chlorine (3.0 on Pauling's scale) a positive charge on the carbon should be destabilized more by fluorine than by chlorine. In fact, CCl_3^+ has been isolated by matrix isolation at -196°. Thus, from an electronegativity viewpoint, the fluorochloromethyl cations should have increased stability with decreased fluorine content, as,

$$CCl_3^+ > CFCl_2^+ > CF_2Cl^+ > CF_3^+ \qquad (145)$$

showing the relative stabilities.

A second set of comparative reactions is that of $(CF_2Cl)X$. Again, as Cl^- and F^- are very stable at high pressure in a polar solvent, the

non-reactivity of $(CF_2Cl)F$ is again indicative of the instability of a second cation $(CF_2Cl)^+$, i.e.

$$(CF_2Cl)X + H_2O \rightarrow [H_2O\cdots\cdots\cdots\overset{+}{C}F_2Cl\cdots\cdots\cdots\bar{X}] \qquad (146)$$

This reaction does not proceed by this intermediate. Of the two reactions, $(CF_2Cl)F$ should be favored over $(CF_2Cl)Cl$ with the same R-group because of the large ΔV_o^* of F^-. The reverse of this is observed.

With the previous conclusions, a third set of comparative reactions can be considered, that of $(CFCl_2)F$ and $(CFCl_2)Cl$. As previously indicated, the ratio of reactivity of $(CFCl_2)F$ and $(CFCl_2)Cl$ toward H_2O is about 4:1, viz.

$$(CFCl_2)X + H_2O \rightarrow [H_2O\cdots\cdots\cdots\overset{+}{C}FCl_2\cdots\cdots\cdots\bar{X}] \qquad (147)$$

The fact that this reaction proceeds by this transition state indicates that $(CFCl_2)^+$ is a stable ionic intermediate. The greater reactivity of $(CFCl_2)F$ under pressure can be explained if there is more bond breaking (R-X) than bond making (Y-R) in the transition state taking advantage of the greater ΔV_o^* of fluorine than of chlorine, i.e. on S_N1 mechanism where the rate determining step is,

$$(CFCl_2)X \rightarrow CFCl_2^+ + X^- \qquad (148)$$

$$H_2O + CFCl_2^+ \rightarrow \overset{+}{H}_2O\text{-}CFCl_2 \qquad (149)$$

As indicated by other workers[52,125], this reaction can then proceed as follows,

$$\overset{+}{H}_2O\text{-}CFCl_2 \rightarrow H^+ + (HO\text{-}CFCl_2) \qquad (150)$$

with subsequent loss of HCl or HF from this trihaloalcohol,

$$HO\text{-}CFCl_2 \rightarrow HCl + ClFCO \qquad (151)$$

$$(or) \rightarrow HF + Cl_2CO \qquad (152)$$

followed by the well known hydrolysis of the halocarbonyls,

$$Cl_2CO + H_2O \rightarrow 2\ HCl + CO_2 \quad (153)$$

$$(or)\ ClFCO + H_2O \rightarrow HF + HCl + CO_2 \quad (154)$$

Finally, a comparison of the rates of hydrolysis of $(CCl_3)F$ and $(CCl_3)Cl$ can be fruitful. The rate of hydrolysis of $(CCl_3)F$ at high pressure and 300°. This indicates that the intermediate $(CCl_3)^+$ is a stable species, viz.

$$(CCl_3)X + H_2O \rightarrow [H_2O\cdots\cdots\cdots\overset{+}{C}Cl_3\cdots\cdots\cdots X] \quad (155)$$

The ion CCl_3^+ has been isolated by trapping the products of CCl_4 pyrolysis at high temperature (900°) in a -196° trap[153]. The greater reactivity of $(CCl_3)Cl$ in this pair of reactions can best be interpreted by simultaneous bond breaking (R-X) and bond making (Y-R), i.e. an S_N2 mechanism. The S_N2 mechanism for the hydrolysis of CCl_4 could be represented as follows,

$$CCl_4 + H_2O \rightarrow [H_2O\cdots\cdots\cdots\overset{+}{C}Cl_3\cdots\cdots\cdots\bar{C}l] \quad (156)$$

with subsequent loss of HCl,

$$[H_2O\cdots\cdots\cdots\overset{+}{C}Cl_3\cdots\cdots\cdots\bar{C}l] \rightarrow HO\text{-}CCl_3 + HCl \quad (157)$$

From this step, the trihaloalcohol rearranges to HCl and Cl_2CO which further hydrolyzes to HCl and CO_2 as in the $(CFCl_2)F$ mechanism.

It only remains to propose a mechanism for the hydrolysis of $(CCl_3)F$. In view of slower rate of hydrolysis of $(CCl_3)F$ compared to $(CCl_3)Cl$ (S_N2) and $(CFCl_2)F$ (S_N1), the rate of hydrolysis of $(CCl_3)F$ or $(CFCl_2)Cl$ can best be explained as a limiting case of the S_N2 mechanism. The CCl_3^+ from $(CCl_3)F$ species should be more stable than the $CFCl_2^+$ species from $(CFCl_2)F$ because of lower fluorine content, thus with F^- being the other ionic product of the S_N1 mechanism proposed for each, viz.

$$(CCl_3)F \rightarrow CCl_3^+ + F^- \quad (158)$$

$$\text{and } (CFCl_2)F \rightarrow CFCl_2^+ + F^- \quad (159)$$

the two should react at near equal rates by an S_N1 mechanism, not the 4:1 ratio observed. This implies that $(CCl_3)F$ does not react by an S_N1 mechanism.

It only remains to conclude that $(CCl_3)F$ reacts by an S_N2 mechanism, the same as CCl_4, viz.

$$(CCl_3)F + H_2O \rightarrow [H_2O\cdots\cdots\overset{+}{C}Cl_3\cdots\cdots\bar{F}] \quad (160)$$

with subsequent reaction to HCl and CO_2 as indicated by the CCl_4 mechanism.

The slower rate of hydrolysis of $(CCl_3)F$ compared to CCl_4 can be attributed by this mechanism to slow cleavage of the C-F bond compared to the C-Cl bond due to the greater bond strength of the C-F bond[51].

The final question to be considered is why wasn't HF detected in the products of the $CFCl_3$ and CF_2Cl_2 hydrolysis. As indicated in the summary, SiF_4 was observed in several mass spectra of the above reaction products which could have been formed from the reaction of HF and SiO_2. The mass spectrum of HF should be extremely weak due to the high electronegativity of fluorine and the resultant instability of the cations, HF^+ and F^+ in the positive ion mass spectrum. Another possibility is that the HF formed reacted with the fluorochloromethanes to form the higher fluorinated derivative, as with CF_2Cl_2,

$$CF_2Cl_2 + HF \rightarrow CF_3Cl + HCl \quad (161)$$

It is well established that HF will directly fluorinate fluorochloromethanes under pressure. In a gold tube, it is possible that the fluo-

rination is catalyzed by the Au as AuF_2[64] has been used as a fluorination catalyst.

The mechanisms proposed are in agreement with the experimental results. These reactions do need to be studied in more detail to determine if the mechanisms vary with temperature and to see what effect the amount of H_2O has on the rates and extents of hydrolysis.

D. The Photochemical Substitution of PF_3 for CO.

The total substitution of CO by PF_3 in a transition metal carbonyl is at best a very difficult task. Clark[36] has studied the preparation and properties of these mixed ligand coordination compounds extensively. Their separation and purification has involved all phases of chromatography, depending on the particular air, thermal, and photochemical stability of the complex mixture under study.

In a private communication, MacDiarmid[92] has indicated that in the thermal reaction of $Cl_3Si\text{-}Co(CO)_4$ and PF_3 at 100° under an autogenous pressure of 12 atmospheres that monosubstitution of PF_3 for CO occurred within 4 hours with about 5% disubstitution occurring (i.e., $Cl_3Si\text{-}Co(CO)_3PF_3$ and $Cl_3Si\text{-}Co(CO)_2(PF)_2$ being formed).

1. Summary. In an attempt to form the tetra-substituted substance, $Cl_3Si\text{-}Co(PF_3)_4$, a preliminary experiment was carried out where the corresponding carbonyl compound ($Cl_3Si\text{-}Co(CO)_4$) was combined with PF_3 at 50° and 40 atmospheres with uv irradiation for a total of 12 hours. Every two hours the reaction was quenched in liquid nitrogen and the evolved CO pumped off. The reaction was attempted at room temperature without success. As the melting point of $Cl_3SiCo(CO)_4$ is

45°, the liquid phase is apparently necessary for reaction to occur. The reaction mixture changed from a light yellow liquid to a deep red liquid in less than 1 hour. The deep red liquid remained when the mixture was cooled to room temperature.

The gas phase infrared spectrum indicates the presence of coordinated CO and PF_3 in the red liquid. The presence of the $SiCl_3$ group is also indicated. A preliminary Fluorine-19 NMR agrees with the reported chemical shift values of MacDiarmid[93], but the spectrum is apparently much more complicated than his reported values for the mono- and di- substituted species.

The final attempt to determine the exact nature of the substitution product was a room temperature mass spectrum. When the ion source of the mass spectrometer was operated above 50°, the spectrum obtained was consistent with a mixture of the general formula $Cl_3Si\text{-}Co(CO)_x(PF_3)_{3-x}$ containing only three ligands instead of the usual four for this class of cobalt(I) coordination compounds. As indicated in Table VI, when the ion source and inlet are below 50°, a new and unique addition to the previous spectral peaks is observed. Rather than obtaining spectral peaks corresponding to four ligands on each cobalt as expected, a whole new series of peaks appeared that corresponded to the dimer of the higher temperature spectrum corresponding to $[Cl_3Si\text{-}Co(CO)_x(PF_3)_{3-x}]_2$. As an added indication of the proposed formula, the dimer mass spectral peaks have the isotopic pattern of 6 chlorine atoms (m, 50%; m+2, 100%; m+4, 83%; m+6, 37%; m+8, 9.25%; m+8, 1.2%) as compared to the higher temperature lower molecular weight spectrum with the 3 chlorine atom (m, 100; m+2, 98%; m+4, 31%) isotopic patterns. None of the other

atoms included have more than one significant naturally occurring isotope.

This preliminary study supports the use of photochemical as well as thermal means of initiating substitution reactions in inorganic and organometallic chemistry. Unfortunately, the reaction mixture was thermally and possibly photochemically unstable, resulting in significant decomposition and limiting severely the analysis of a very complex but unusual reaction.

CHAPTER IV

SUMMARY

This investigation was undertaken in order to study the use of high pressure in the synthesis of inorganic and organometallic compounds. Several different types of phase pairs (gas-gas, gas-solid, gas-liquid) have been studied in terms of the feasibility of synthetic reactions with some emphasis on evaluating the minimum pressure necessary to achieve useful syntheses.

Experimental Studies.

1. A new method for the synthesis of $Ni(PF_3)_4$, $Mo(PF_3)_6$ and $W(PF_3)_6$ was developed. These coordination compounds were formed by the reaction of the corresponding transition metal oxides with PF_3 in the presence of Mg at 4000 atmospheres and 300°. The NiO was observed to combine at 100 atmospheres and 300° to yield the $Ni(PF_3)_4$.

2. A method of reducing transition metal oxides at high pressure was developed such that,

$$MO_x + (x-y)PF_3 \rightarrow MO_y + (x-y)OPF_3 \qquad (162)$$

where M = Cr, Ta, Ru, Os, Zr, V, Ti, Fe and Co. This series of reaction was observed at 4000 atmospheres and 300°.

3. Four new syntheses of OPF_3 were developed:

a. The reaction of transition metal oxides and PF_3 at

4000 atmospheres and 300°.

b. The reaction of O_2 and PF_3 at 4000 atmospheres and 300°.

c. The reaction of PF_5 and O_2 in the presence of Mg at 1 atmosphere and 300° for 15 minutes.

d. The reaction of PF_5 and MgO at 1 atmosphere and 300° for 2 hours.

4. Two unique syntheses of $P_2O_3F_4$ were developed:

a. The reaction of O_2 and PF_3 (or OPF_3) with Mg at 4000 atmospheres and 300°.

b. The reaction of O_2 and PF_5 with Mg at 1 atmosphere and 300° for 2 hours.

5. Phosphorus trifluoride was observed to react with Group VIA elements to yield the product XPF_3, (X = 1/2 O_2, S, Se) at 4000 atmospheres and 300°. Tellurium was not observed to react with PF_3 at the same conditions, but did alloy the gold tubing.

6. Selected fluorochloromethanes were observed to hydrolyze above 200 atmospheres at 300°.

a. The halomethanes, CCl_4, $CFCl_3$, and CF_3Cl_2, reacted with H_2O to form HCl, CO_2 and higher fluorine content species up to CF_3Cl. No CF_4 was observed.

b. The halomethanes, CF_3Cl and CF_4, did not undergo reaction, even at 4000 atmospheres and 300°.

7. At 4000 atmospheres and 300°, $CFCl_3$ was observed to rearrange to CF_2Cl_2 and CCl_4 with 60% rearrangement in 12 hours. However, only 5% rearrangement of CF_2Cl_2 to $CFCl_3$ and CF_3Cl is observed under the same conditions.

8. A preliminary study was attempted on the photochemical substitution of PF_3 for CO in $Cl_3Si\text{-}Co(CO)_4$ using PF_3 under an autogenous pressure of 40 atmospheres to favor the PF_3 substituted derivative ($Cl_3Si\text{-}Co(PF_3)_4$). The preliminary results indicate that a more complex species is observed, perhaps a dimer.

Appendix A.

The figure below is a schematic diagram of the high pressure-high vacuum system designed by J. J. Moscony, R. I. Harker, and A. G. MacDiarmid.[113]

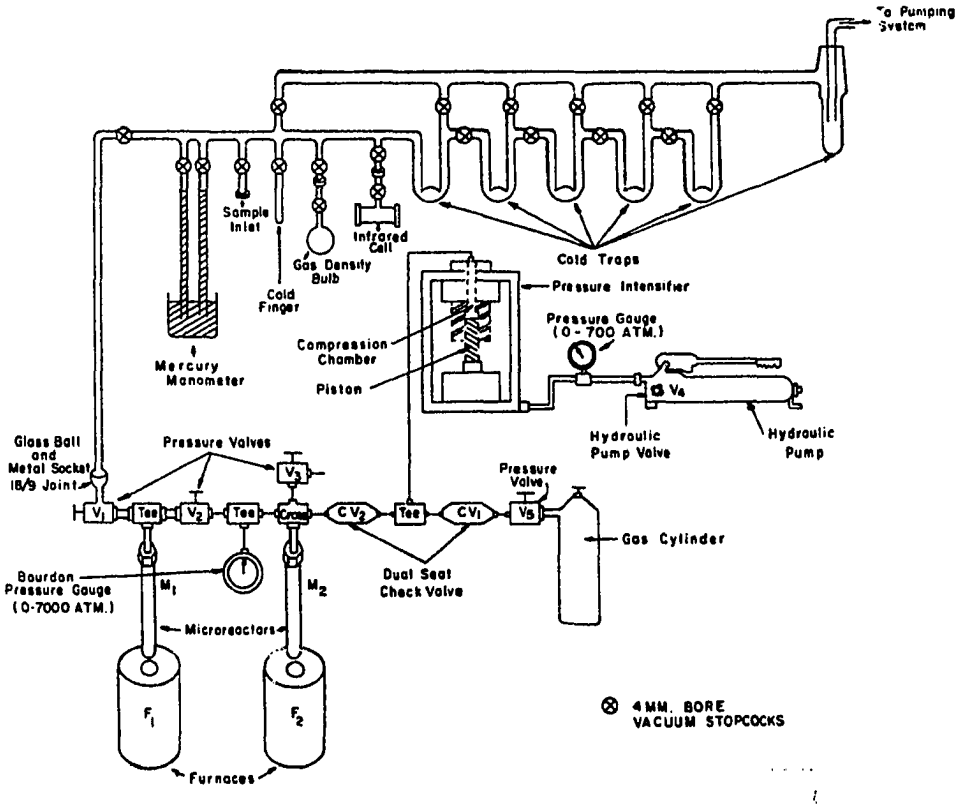


Figure 6. Diagram of High-Pressure System

Appendix B

WORKING LIMITS OF GLASS PRESSURE VESSELS

It has been shown that the maximum pressure a vessel will withstand before bursting is a function of the tensile strength of the construction material and the object's geometry. For a thin walled cylindrical container the approximate maximum pressure which the side walls can withstand is given by the equation,[28]

$$P = \sigma \left[\frac{O.D.}{I.D.} - 1\right] \tag{163}$$

where p = pressure

σ = tensile strength

O.D. = outside diameter

I.D. = inside diameter

For a thin walled cylinder, it can be shown that the longitudinal stress is less than the circumferential stress, thus making the circumferential stress the limiting factor for safe pressure limits. The tensile strength of pyrex glass may be taken as 120 atmospheres for temperatures up to 200°[68]. Table VII presents several "safe" pressure levels for glass vessels, however extreme caution should be used whenever a pressure differential is applied across a glass surface.

TABLE VII

Ideal Internal Pressure Limits of Glass Vessels as Used in This Research

O.D. (mm.)	I.D. (mm.)	Wall (mm.)	Pressure (atmospheres)
22	19	1.5	19
22	18	2.0	28
22	14	4.0	74
14	11	1.2	28
14	10	2.0	52
14	8	3.0	98

Appendix C

Mass Spectral Data

Phosphorus Trifluoride

m/e	I	I/I_o	% T.I.C.[a]	Species
88	7.5	37.6	37.6	PF_3^+
69	20.0	100.0	62.1	PF_2^+
50	2.7	13.4	8.3	PF^+
31	1.7	8.8	5.6	P^+
19	0.2	1.0	0.6	F^+

[a] T.I.C. = total ion current

Appendix D

Mass Spectral Data

Fluorochloromethanes

Spectra 1 - Carbon Tetrachloride

m/e	I	I/I_o	% T.I.C.[a]	Species
12	1.3	2.5	0.7	C^+
35	7.6	14.8	4.3	Cl^+
36	1.7	3.3	1.0	HCl^+
37	2.5	4.9	1.4	Cl^+
38	0.4	0.8	0.2	HCl^+
47	12.3	24.0	6.9	CCl^+
49	4.2	8.2	2.4	CCl^+
82	15.3	29.8	8.6	CCl_2^+
84	10.2	19.9	5.8	CCl_2^+
86	1.4	2.7	0.8	CCl_2^+
117	51.3	100%	29.0	CCl_3^+
119	48.6	94.7	27.4	CCl_3^+
121	18.0	35.1	10.2	CCl_3^+
123	2.2	4.3	1.2	CCl_3^+

[a] T.I.C. = total ion current.

Appendix D

Mass Spectral Data

Fluorochloromethanes

Spectra 2 - Trichlorofluoromethane

m/e	I	I/I_o	% T.I.C.[a]	Species
12	1.1	1.5	0.5	C^+
31	9.9	13.6	4.3	CF^+
35	11.2	15.4	4.9	Cl^+
36	2.0	2.7	0.9	HCl^+
37	4.0	5.4	1.7	Cl^+
38	0.8	1.1	0.3	HCl^+
47	9.8	13.4	4.2	CCl^+
49	3.4	4.7	1.5	CCl^+
50.5	2.6	3.6	1.1	$CFCl_2^+$
51.5	1.2	1.6	0.5	$CFCl_2^{++}$
52.5	0.4	0.5	0.2	$CFCl_2^{++}$
66	15.9	21.8	6.9	$CFCl^+$
68	5.3	7.3	2.3	$CFCl^+$
70	0.6	0.8	0.2	$CFCl^+$
82	4.6	6.3	2.0	CCl_2^+
84	3.2	4.4	1.4	CCl_2^+
86	0.8	1.1	0.3	CCl_2^+
101	72.9	100%	31.5	$CFCl_2^+$
102	1.2	1.6	0.5	$CFCl_2^+$

Trichlorofluoromethane - continued

m/e	I	I/I_o	% T.I.C.[a]	Species
103	59.4	81.5	25.7	$CFCl_2^+$
104	0.8	1.1	0.3	$CFCl_2^+$
105	14.1	19.3	6.1	$CFCl_2^+$
117	2.9	4.0	1.3	CCl_3^+
119	2.3	3.2	1.0	CCl_3^+
121	0.8	1.1	0.3	CCl_3^+

[a] T.I.C. = total ion current.

Appendix D

Mass Spectral Data

Fluorochloromethanes

Spectra 3 - Dichlorodifluoromethane

m/e	I	I/I_o	% T.I.C.[a]	Species
12	1.1	1.4	0.5	C^+
31	9.0	11.4	4.4	CF^+
35	8.3	10.5	4.1	Cl^+
36	1.3	1.6	0.6	HCl^+
37	2.4	3.0	1.2	Cl^+
38	0.6	0.7	0.3	HCl^+
47	4.4	5.5	2.1	CCl^+
49	1.0	1.34	0.5	CCl^+
50	16.2	20.4	7.9	CF_2^+
50.5	0.7	0.9	0.3	$CFCl_2^{++}$
51	0.5	0.6	0.2	$CFCl_2^{++}$
51.5	0.4	0.5	0.2	CF_2^+
66	5.0	6.3	2.5	$CFCl^+$
68	1.6	2.0	0.8	$CFCl^+$
85	79.2	100%	38.9	CF_2Cl^+
86	1.8	2.3	0.9	CF_2Cl^+
87	46.8	59.1	23.0	CF_2Cl^+
101	12.6	15.9	6.2	$CFCl_2^+$
103	8.0	10.1	3.9	$CFCl_2^+$
105	1.5	1.9	0.7	$CFCl_2^+$

Dichlorodifluoromethane - continued

m/e	I	I/I_o	% T.I.C.[a]	Species
120	0.6	0.8	0.3	$CF_2Cl_2^+$
122	0.5	0.6	0.2	$CF_2Cl_2^+$

[a] T.I.C. = total ion current.

Appendix D

Mass Spectral Data

Fluorochloromethanes

Spectra 4 - Chlorotrifluoromethane

m/e	I	I/I_o	% T.I.C.[a]	Species
12	1.4	1.4	0.7	C^+
31	5.1	5.2	2.6	CF^+
35	9.1	9.3	4.7	Cl^+
36	0.7	0.7	0.4	HCl^+
37	2.2	2.2	1.1	Cl^+
38	0.3	0.3	0.1	HCl^+
42.5	3.7	3.8	1.9	CF_2Cl^{++}
43.5	1.4	1.4	0.7	CF_2Cl^{++}
47	1.1	1.1	0.6	$CFCl^+$
49	0.3	0.3	0.1	$CFCl^+$
50	15.3	15.6	7.9	CF_2^+
66	0.7	0.7	0.3	$CFCl^+$
68	0.2	0.2	0.1	$CFCl^+$
69	98.1	100%	50.6	$C^{12}F_3^+$
70	2.4	2.4	1.2	$C^{13}F_3^+$
85	37.8	38.5	19.5	CF_2Cl^+
87	12.0	12.0	6.1	CF_2Cl^+
104	2.1	2.1	1.1	CF_3Cl^+
106	0.5	0.5	0.2	CF_3Cl^+

[a] T.I.C. = total ion current.

Appendix D

Mass Spectral Data

Fluorochloromethanes

Spectra 5 - Carbon Tetrafluoride

m/e	I	I/I_o	% T.I.C.[a]	Species
12	2.6	2.9	2.1	C^+
19	2.25	2.5	1.8	F^+
25	3.1	3.4	2.5	CF_2^{++}
31	4.1	4.5	3.3	CF^+
34.5	1.5	1.6	1.2	CF_3^{++}
50	17.1	18.8	13.7	CF_2^+
69	90.9	100%	72.8	CF_3^+
70	3.2	3.5	2.5	$C^{13}F_3^+$

[a] T.I.C. = total ion current.

Appendix E

Mass Spectral Data

Phosphoryl Fluorides

Spectra 1 - Phosphoryl Fluoride

m/e	I	I/I_o	% T.I.C.[a]	Species
47	0.7	2.2	1.2	PO^+
50	0.8	2.5	1.3	PF^+
69	3.7	11.4	6.1	PF_2^+
85	23.4	72.2	38.3	OPF_2^+
104	32.4	100%	53.1	OPF_3^+

[a] T.I.C. = total ion current.

Appendix E

Mass Spectral Data

Phosphoryl Fluorides

Spectra 2 - Thiophosphoryl Fluoride

m/e	I	I/I_o	% T.I.C.[a]	Species
18	2.5	2.8	1.4	H_2O^+
31	1.5	1.7	0.9	P^+
32	12.3	10.0	5.1	S^+
34	1.5	1.7	0.9	S^+
50	3.5	4.0	2.0	PF^+
63	1.5	1.7	0.9	PS^+
64	3.4	3.9	2.0	SO_2^+
69	19.5	22.1	11.2	PF_2^+
85	2.9	3.3	1.7	OPF_2^+
88	5.8	6.6	3.3	PF_3
101	21.6	24.4	12.2	SPF_2^+
103	1.0	1.1	0.6	SPF_2^+
104	4.0	4.5	2.3	OPF_3^+
120	88.2	100%	50.7	SPF_3^+
121	1.3	1.5	0.8	SPF_3^+
122	6.9	7.8	4.0	SPF_3^+

[a] T.I.C. = total ion current.

Appendix E

Mass Spectral Data

Phosphoryl Fluorides

Spectra 3 - Selenophosphoryl Fluoride[b]

m/e	I	I/I_o	% T.I.C.[a]	Species
31	0.7	2.6	1.0	P^+
50	3.2	12.1	4.6	PF^+
69	15.0	56.8	21.4	PF_2^+
80	7.0	26.7	10.1	Se^+
85	3.9	14.8	5.6	OPF_2^+
88	5.7	21.6	8.2	PF_3^+
104	3.7	14.0	5.3	OPF_3^+
111	0.5	1.9	0.7	SeP^+
130	0.3	1.1	0.4	$SePF^+$
149	3.5	13.3	5.0	$SePF_2^+$
168	26.4	37.8	100%	$SePF_3^+$

[a] T.I.C. = total ion current.

[b] Monoisotopic mass spectrum for $^{80}_{34}Se$.

Appendix E

Mass Spectral Data

Phosphoryl Fluorides

Spectra 4 - Difluorophosphoric Acid

m/e	I	I/I_o	% T.I.C.[a]	Species
102	13.8	100	27.4	$HO_2PF_2^+$
85	12.0	90.6	24.8	OPF_2^+
83	7.9	57.2	15.7	HO_2PF^+
82	2.0	14.5	4.0	O_2PF^+
6	2.7	18.1	5.0	PF_2
63	3.7	26.8	7.3	PO_2^+
50	1.5	10.5	2.9	PF^+
47	3.5	25.1	6.9	PO^+
31	1.2	8.7	2.4	P^+
67	0.8	5.8	1.6	$HOPF^+$
66	1.0	7.2	2.0	OPF^+

[a] T.I.C. = total ion current.

Appendix E

Mass Spectral Data

Phosphoryl Fluorides

Spectra 5 - μ-Oxo-bisdifluorophosphoryl

m/e	I	I/I_o	% T.I.C.[a]	Species
186	15.6	67.5	24.5	$P_2O_3F_4^+$
167	2.5	10.8	3.9	$P_2O_3F_4^+$
104	3.4	14.7	5.3	OPF_3^+
103	3.5	15.1	5.5	$H_2O{\cdot}POF_2^+$ [b]
102	3.4	14.7	5.3	$HO{\cdot}POF_2^+$ [b]
85	23.1	100%	36.3	OPF_2^+
83	1.7	7.4	2.7	O_2PF^+
82	2.0	8.6	3.1	$H_2O{\cdot}OP^+$ [b]
69	3.5	15.1	5.5	PF_2^+
67	0.2	0.8	0.3	OPF^+
66	0.8	3.5	1.3	$H_2O{\cdot}OP^+$ [b]
63	0.9	3.9	1.4	PO_2^+
50	0.7	3.0	1.1	PF^+
47	1.9	8.2	3.0	PO^+
31	0.3	1.3	0.5	P^+
16	0.2	0.8	0.3	O^+

[a] T.I.C. = total ion current.

[b] Result of reaction of H_2O in the mass spectrometer.

Appendix F

Mass Spectral Data

Spectra 1 - Tetrakis(trifluorophosphine)nickel[b]

m/e	I	I/I_o	% T.I.C.[a]	Species
58	17.40	57.1	16.9	Ni^+
127	1.19	3.91	1.2	$Ni(PF_2)^+$
146	30.5	100	29.6	$Ni(PF_3)^+$
165	1.31	4.29	1.3	$Ni(PF_3F)^+$
215	3.23	10.60	3.1	$Ni(PF_3)PF_2^+$
234	23.04	75.6	22.4	$Ni(PF_3)_2^+$
303	5.50	18.04	5.3	$Ni(PF_3)_2PF_2^+$
322	19.14	6.28	18.6	$Ni(PF_3)_3^+$
410	1.70	5.58	1.6	$Ni(PF_3)_4^+$

[a] T.I.C. = total ion current.

[b] Monoisotopic mass spectrum for $^{58}_{28}Ni$.

Appendix F

Mass Spectral Data

Spectra 2 - Hexakis(trifluorophosphine)molybdenum[b]

m/e	I	I/I_o	% T.I.C.[a]	Species
626	5.90	22.78	6.6	$Mo(PF_3)_6^+$
607	0.42	1.62	0.5	$Mo(PF_3)_5PF_2^+$
538	0.88	3.39	1.0	$Mo(PF_3)_5^+$
519	4.83	18.65	5.3	$Mo(PF_3)_4PF_2^+$
469	0.62	2.39	0.7	$Mo(PF_3)_4F^+$
450	3.21	12.39	3.6	$Mo(PF_3)_4^+$
431	3.40	13.13	3.8	$Mo(PF_3)_3PF_2^+$
362	6.94	26.80	7.7	$Mo(PF_3)_3^+$
343	3.86	14.90	4.3	$Mo(PF_3)_2PF_2^+$
274	11.02	42.56	12.2	$Mo(PF_3)_2^+$
255	2.03	7.84	2.2	$Mo(PF_3)PF_2^+$
186	25.89	100.00	28.8	$Mo(PF_3)_1^+$
117	5.48	21.16	6.1	MoF^+
98	15.63	60.37	17.4	Mo^+

[a] T.I.C. = total ion current.

[b] Monoisotopic mass spectrum for $^{98}_{42}Mo$.

Appendix F

Mass Spectral Data

Spectra 3 - Hexakis(trifluorophosphine)tungsten[b]

m/e	I	I/I_o	% T.I.C.[a]	Species
712	9.62	51.88	13.6	$W(PF_3)_6^+$
693	2.50	13.48	3.5	$W(PF_3)_5PF_2^+$
624	2.20	11.866	3.1	$W(PF_3)_5^+$
605	5.52	29.77	7.8	$W(PF_3)_4PF_2^+$
536	4.80	25.88	6.8	$W(PF_3)_4^+$
517	3.23	17.42	4.6	$W(PF_3)_3PF_2^+$
467	1.00	5.39	1.4	$W(PF_3)_3F^+$
448	9.18	49.51	13.0	$W(PF_3)_3^+$
429	2.13	11.48	3.0	$W(PF_3)_2PF_2^+$
410	0.28	1.51	0.4	$W(PF_3)_2PF^+$
379	1.16	6.25	1.6	$W(PF_3)_2F^+$
360	5.87	31.66	8.3	$W(PF_3)_2^+$
291	2.91	15.69	4.1	$W(PF_3)F^+$
272	18.54	100.00	26.3	$W(PF_3)^+$
184	1.55	8.36	2.2	W^+

[a] T.I.C. = total ion current.

[b] Monoisotopic mass spectrum for $^{184}_{74}W$.

Appendix G

Mass Spectral Data

$Cl_3SiCo(CO)_4$ [b]

m/e	I	I/I_o	% T.I.C.[a]	Species
304	0.2	1.02	0.2	$Cl_3SiCo(CO)_4^+$
276	3.8	17.8	3.4	$Cl_3SiCo(CO)_3^+$
269	0.9	4.7	0.9	$Cl_2Si\text{-}Co(CO)_4^+$
248	7.3	38.0	7.3	$Cl_3SiCo(CO)_2^+$
241	0.7	3.6	0.7	$Cl_2SiCo(CO)_3^+$
220	19.2	100	19.2	$Cl_3SiCo(CO)^+$
213	0.4	2.1	0.4	$Cl_2SiCo(CO)_2^+$
192	9.7	50.5	9.7	Cl_3SiCo^+
185	0.9	4.6	0.9	$Cl_2SiCo(CO)^+$
171	0.4	2.1	0.4	$Si\text{-}Co(CO)_3^+$
157	2.5	13.0	2.5	Cl_2SiCo^+
143	1.3	6.7	1.3	$SiCo(CO)_2^+$
133	2.0	10.2	2.0	Cl_3Si^+
121	1.9	9.9	1.9	$ClSiCo^+$
115	5.3	27.6	5.3	$SiCo(CO)^+$
98	2.3	12.0	2.3	Cl_2Si^+
94	1.2	6.3	1.2	$ClCo^+$
87	7.4	38.6	7.4	$SiCo^+$
71	0.9	4.7	0.9	CoC^+

$Cl_3SiCo(CO)_4$ - continued

m/e	I	I/I_o	% T.I.C.[a]	Species
63	18.6	97	18.7	$SiCl^+$
59	11.3	58.9	11.3	Co^+
35	2.0	10.2	2.0	Cl^+

[a] T.I.C. = total ion current

[b] Monoisotopic mass spectrum for $^{35}_{17}Cl$.

BIBLIOGRAPHY

1. Am. Petro. Inst. Res. Proj. 44, Serial 93.
2. Am. Petro. Inst. Res. Proj. 44, Serial 401.
3. Am. Petro. Inst. Res. Proj. 44, Serial 603.
4. Am. Petro. Inst. Res. Proj. 44, Serial 1582.
5. Am. Petro. Inst. Res. Proj. 44, Serial 1641.
6. Am. Petro. Inst. Res. Proj. 44, Serial 1642.
7. Appendix E, Spectra 3, This Dissertation.
8. Appendix E, Spectra 5, This Dissertation.
9. Appendix F, Spectra 1, This Dissertation.
10. Appendix F, Spectra 2, This Dissertation.
11. Appendix F, Spectra 3, This Dissertation.
12. Appendix G, This Dissertation.
13. E. E. Aynsley, R. Nichols and P. L. Robinson, J. Chem. Soc., 623 (1953).
14. Y. L. Baay, Ph.D. Dissertation, University of Pennsylvania, Philadelphia, Pennsylvania, 1967.
15. G. Balz and E. Mailander, Z. Anorg. Allg. Chem., 217, 161 (1934).
16. A. K. Barbour, L. J. Belf, and M. W. Buxton, Advances in Fluorine Chemistry, Vol. 3., M. Stacey, J. C. Tatlow, and A. G. Sharp, Butterworth Inc., Washington, D. C., 1963, p. 181.
17. E. Baudriment, Ann. Chim. Phys., 2, 5 (1864).
18. J. Berak, Roczn, Chem., 36, 403 (1962).

19. J. Berak and I. Tomczak, Roca. Chem., 39, 1961 (1965).

20. P. A. Bernstein, F. A. Hohorst, M. Eisenberg and D. MesMarteau, Inorg. Chem., 10, 1549 (1971).

21. M. Bigorgne and A. Zelwer, Bull. Soc. Chim. Fr., 1986 (1960).

22. H. S. Booth and A. R. Bozarth, J. Amer. Chem. Soc., 61, 2927 (1939).

23. H. S. Booth and M. P. Cassidy, J. Amer. Chem. Soc., 62, 2369 (1940).

24. H. S. Booth and F. B. Dutton, J. Amer. Chem. Soc., 61, 2937 (1939).

25. H. S. Booth and C. A. Seabright, J. Amer. Chem. Soc., 65, 1834 (1943).

26. H. S. Booth and C. F. Swinehart, J. Amer. Chem. Soc., 54, 4751 (1932).

27. H. S. Booth and J. H. Walkup, J. Amer. Chem. Soc., 65, 2334 (1943).

28. R. S. Bradley and D. C. Munro, High Pressure Chemistry, Pergamon Press, Oxford, 1965.

29. R. G. Cavell, Can. J. Chem., 46, 613 (1968).

30. M. Chaigneau and M. Santarromana, C. R. Acad. Sci. Paris, 268(C), 825 (1969).

31. M. M. Chaigneau and M. Santarromana, C. R. Acad. Sci. Paris, 269(C), 1943 (1969).

32. A. J. Chalk and J. F. Harrod, J. Amer. Chem. Soc., 87, 1133 (1965).

33. G. Chandron, Presented at IUPAC-Symposium 'Silizium-Schwefel-Phosphate' Munster 1954, Abstr. p. 172.

34. J. Chatt, Nature, 165, 637 (1950).

35. J. Chatt and A. Williams, J. Chem. Soc., 3061 (1951).

36. R. J. Clark, Inorg. Chem., 3, 1395 (1964).

37. R. Clement and L. Benck, A. Anorg. Allg. Chem., 287, 12 (1956).

38. E. W. Comings, High Pressure Technology, McGraw-Hill, New York, 1956, p. 410.

39. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Interscience Publishers, New York, 1956.

40. G. A. Crowder, J. Chem. Phys., 49, 4622 (1968).

41. B. F. Dodge, High Pressure Physics and Chemistry, Vol. 2., R. S. Bradley, Academic Press Inc., New York, 1963, p. 91.

42. A. Drude and W. Nernst, Z. Phys. Chem. (Leipzig), 15, 79 (1894).

43. E. I. DuPont DeNemours and Co., Belg. Pat. No. 621, 364 (1962).

44. F. Ebel and E. Bretscher, Helv. Chim. Acta, 12, 450 (1929).

45. B. J. Eiseman, Chem. and Eng. News, 39, 44 (1961).

46. A. J. Ellis, J. Chem. Soc., 3689 (1957).

47. A. J. Ellis and D. W. Anderson, J. Chem. Soc., 1765 (1961).

48. A. H. Ewald, S. D. Hamman and J. E. Stutchbury, Trans. Faraday Soc., 53, 991 (1957).

49. H. Eyring, A. Sherman and G. E. Kimball, J. Chem. Phys., 1, 586 (1933).

50. I. Fells and E. A. Moelwyn-Hughes, J. Chem. Soc., 1326 (1958).

51. D. C. Frost and C. A. McDowell, Proc. Roy. Soc., A241, 194 (1957).

52. M. S. Gaisinovich and A. N. Ketov, Zh. Neorg. Chim., 14, 2316 (1969).

53. S. Glasstone, K. J. Laidler and H. Erying, Theory of Rate Processes, McGraw-Hill, New York, 1941.

54. M. G. Gonikberg, V. M. Zhulin and B. S. El'yanov, The Physics and Chemistry of High Pressures, Olympia Symposium, Goorden and Breach, New York, 1963, p. 212.

55. J. Goubeau, W. Beus and F. W. Kampmann, Z. Anorg. Allg. Chem., 283, 123 (1956).

56. J. E. Griffiths and A. B. Burg, J. Amer. Chem. Soc., 82, 1507 (1960).

57. E. A. Guggenheim, Trans. Faraday Soc., 33, 607 (1937).

58. A. Guntz, C. R. Acad. Sci., Paris, 103, 58 (1886).

59. H. S. Gutowsky and A. D. Liehr, J. Chem. Phys., 20, 1652 (1952).

60. A. P. Hagen, Ph.D. Dissertation, University of Pennsylvania, Philadelphia, Pennsylvania.

61. A. P. Hagen and A. G. MacDiarmid, Inorg. Nucl. Chem. Lett., 6, 413 (1970).

62. M. L. Hair and P. L. Robinson, J. Chem. Soc., 106 (1958).

63. S. D. Hamann, High Pressure Physics and Chemistry, Vol. 2., R. S. Bradley, Academic Press Inc., New York, 1963, p. 131.

64. J. M. Hamilton, Advances in Fluorine Chemistry, Vol. 3., M. Stacey, J. C. Tatlow and A. G. Sharp, Butterworth Inc., Washington, D. C., 1963, p. 117.

65. T. Hayashi, Kagyo Kagaku Zusshi, 68(10), 2002 (1965).

66. E. Hayek, A. Aignesberger and A. Engelbrecht, Mh. Chem., 86, 735 (1955).

67. E. Hayek, J. Puschmann and A. Czaloun, Mh. Chem., 85, 359 (1954).

68. G. P. Helliwell, J. Chem. Educ., 41, 575 (1964).

69. G. Herzberg, Molecular Spectra and Molecular Structure, Vol. II, "Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, New York, 1945, p. 322.

70. W. Hieber, Chemie, 55, 24 (1942).

71. W. Hieber, Angew. Chem., 55, 1 (1942).

72. M. E. Hill, J. Org. Chem., 25, 1115 (1960).

73. C. J. Hoffman, Lockhead Missles and Space Division, Tech. Rep. LMSD - 49771, (1959).

74. R. R. Holmes and R. P. Wagner, J. Amer. Chem. Soc., 84, 357 (1962).

75. K. H. Homann and D. I. MacLean, Combust. Flame, 14, 409 (1970).

76. J. B. Hyne, private communication to W. J. le Noble, Prog. in Phy. Org. Chem., Vol. 5., A. Streitwieser and R. W. Taft, Interscience Publishers, New York, 1967, p. 207.

77. W. L. Jolly, The Synthesis and Characterization of Inorganic Compounds, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1970.

78. S. F. A. Kettle and J. A. Khan, J. Organometal. Chem., 5, 588 (1966).

79. R. W. Kiser, J. G. Dillard and D. L. Dugger, Advances in Chemistry Series, Vol. 72., 1968, p. 153.

80. S. Kongprich and W. Preusse, Inorg. Chem., 6, 1915 (1967).

81. T. Kruck, Angew. Chem. Internat. Edit., 6, 53 (1967).

82. T. Kruck, Z. Naturforsch, 19b, 165 (1964).

83. T. Kruck and K. Baur, Chem. Ber., 98, 3070 (1965).

84. T. Kruck, K. Baur and W. Lang, Chem. Ber., 101, 138 (1968).

85. T. Kruck and W. Lang, Angew. Chem. Intl. Edit., 6, 454 (1967).

86. T. Kruck, W. Lang and A. Engelmann, Angew. Chem., 77, 132 (1965).

87. W. Kwasnik, Fluoverbindungen, in G. Brauer, Handbuch der Praparativen Anorganischen Chemie, 2. Auflage, 1. Band., Stuttgart, 1960, p. 182.

88. W. Lange and R. Livingston, J. Amer. Chem. Soc., 72, 1280 (1950).

89. W. J. le Noble, Progress in Physical Organic Chemistry, 5, A. Streitwieser and R. W. Taft, Interscience Publishers, New York, 1967, p. 207.

90. M. Lustig and J. K. Ruff, Inorg. Chem., 6, 2115 (1967).

91. A. G. MacDiarmid, Private Communication.

92. E. T. McBee and A. D. Welch, U. S. Pat. 2,443,630, 1948.

93. G. Mantel, Abstr. IUPAC-Symposium "Silicium-Schwefel-Phosphate", Munster 1954, Abstr. p. 178.

94. H. Moissan, Ann. Chim. Phys., 6, 433 (1885).

95. H. Moissan, Ann. Chim. Phys., 6, 468 (1885).

96. H. Moissan, Ann. Chim. Phys., 19, 286 (1890).

97. H. Moissan, Ann. Chim. Phys., 6, 24, 224 (1891).

98. H. Moissan, Bull. Soc. Chim. Fr. 3, 4, 260 (1890).

99. H. Moissan, Bull. Soc. Chim. Fr., 5, 454 (1891).

100. H. Moissan, Bull. Soc. Chim. Fr., 5, 456 (1891).

101. H. Moissan, Bull. Soc. Chim. Fr., 5, 458 (1891).

102. H. Moissan, Bull. Soc. Chim. Fr., 5, 880 (1891).

103. H. Moissan, C. R. Acad. Sci., Paris, 99, 655 (1884).

104. H. Moissan, C. R. Acad. Sci., Paris, 100, 272 (1885).

105. H. Moissan, C. R. Acad. Sci., Paris, 102, 763 (1886).

106. H. Moissan, C. R. Acad. Sci., Paris, 102, 1245 (1886).

107. H. Moissan, C. R. Acad. Sci., Paris, 103, 1257 (1886).

108. H. Moissan, C. R. Acad. Sci., Paris, 129, 799 (1899).

109. H. Moissan, J. Prakt. Chem., 30, 142 (1884).

110. G. Montel, Bull. Soc. Chim. Fr., 5, 379 (1952).

111. G. Montel and G. Chaudron, C. R. Acad. Sci., Paris, 233, 318 (1951).

112. J. J. Moscony, Ph.D. Dissertation, University of Pennsylvania, Philadelphia, Pennsylvania.

113. J. J. Moscony, R. I. Harker and A. G. MacDiarmid, Rev. Sci. Instrum., 38, 138 (1967).

114. D. W. Muenow, O. M. Uy, and J. L. Margrave, J. Inorg. Nucl. Chem., 31, 3411 (1969).

115. E. L. Muetterties, T. A. Bither, M. W. Farlow and D. D. Coffman, J. Inorg. Nucl. Chem., 16, 52 (1961).

116. E. L. Muetterties and J. E. Castle, J. Inorg. Nucl. Chem., 18, 148 (1961).

117. A. H. Nielson, T. G. Burke, P. J. H. Woltz, and E. A. Jones, J. Chem. Phys., 20, 596 (1952).

118. J. R. Nielson, H. H. Classen and C. C. Smith, J. Chem. Phys., 18, 326 (1950).

119. A. H. Nielson and R. T. Lagemann, J. Chem. Phys., 22, 36 (1954).

120. J. F. Nixon, Advances in Inorganic Chemistry and Radiochemistry, Vol. 9, Academic Press Inc., New York, 1970, p. 373.

121. K. Nozaki, J. Amer. Chem. Soc., 63, 2681 (1941).

122. T. A. O'Donnell and D. R. Stewart. J. Inorg. Nucl. Chem., 24, 309 (1962).

123. G. A. Olah and A. Oswald, Ann. Chem., 602, 118 (1957).

124. A. L. Oppegard, W. C. Smith, E. L. Muetterties and V. A. Engelhardt, J. Amer. Chem. Soc., 82, 3835 (1960).

125. R. E. Parker, Advances in Fluorine Chemistry, Vol. 3., M. Stacey, J. C. Tatlow and A. G. Sharp, Butterworth Inc., Washington, D. C., 1963, p. 63.

126. M. W. Perrin and E. G. Williams, Proc. Roy. Soc. Ser. A, 159, 162 (1937).

127. K. S. Pitzer and L. Brewer, Thermodynamics, 2nd ed., McGraw-Hill, New York, 1961, p. 103.

128. D. W. Pound. Ger. Pat. No. 865,742 (1953).

129. C. Poulenc, C. R. Acad. Sci., Paris, 113, 75 (1891).

130. E. K. Pyler, Phys. Rev., 39, 77 (1932).

131. E. K. Pyler and E. D. Tidwell, Z. Elecktrochem., 64, 717 (1960).

132. R. P. Rhodes, J. Chem. Educ., 40, 423 (1963).

133. R. F. Robey, J. Cosmetic Chem., 21, 183 (1970).

134. E. A. Robinson, Can. J. Chem., 40, 1725 (1962).

135. H. W. Roesky, Angew Chem., 79, 85 (1967).

136. H. W. Roesky, Chem. Ber., 100, 2147 (1967).

137. H. W. Roesky, Chem. Ber., 101, 636 (1968).

138. O. Ruff, Ber. dt. chem. Ges., 39, 4310 (1906).

139. F. Seel, K. Ballreich and W. Peters, Chem. Ber., 92, 2117 (1959).

140. F. Seel, K. Ballreich, and R. Schmutzler, Chem. Ber., 94, 1173 (1961).

141. F. Seel, K. Ballreich, and R. Schmutzler, Chem. Ber., 95, 199 (1962).

142. F. Seel, H. Jonas, L. Hiehl, and J. Langer, Angew. Chem., 67, 32 (1955).

143. F. Seel and L. Riehl, Z. Anorg. Allg. Chem., 282, 293 (1955).

144. Selected Values of Chemical Thermodynamic Properties, N. B. S. Circ. 500, U. S. Govt. Printing Office, Washington, D. C., (1950).

145. D. Seyforth and D. White, J. Organometal. Chem., 32, 317 (1971).

146. A. Simon, German Patent No. 131,414 (1900).

147. E. Stenhagen, S. Abrahamsson and F. W. McLafferty, Atlas of Mass Spectral Data, Interscience Publishers, New York, p. 1.

148. E. Stenhagen, S. Abrahamsson and F. W. McLafferty, Atlas of Mass Spectral Data, Interscience Publishers, New York, p. 215.

149. E. Stenhagen, S. Abrahamsson and F. W. McLafferty, Atlas of Mass Spectral Data, Interscience Publishers, New York, 292.

150. F. E. Saalfeld and M. V. McDowell, Naval Res. Lab. Report 6639 (1967).

151. H. Schulze, Bull. Soc. Chim. Fr., 35, 173 (1881).

152. J. M. Shreeve, and G. Cady, J. Amer. Chem. Soc., 83, 4521 (1961).

153. R. Steudel, Tetrahedron Lett., 47, 4699 (1967).

154. A. G. Streng, J. Amer. Chem. Soc., 85, 1380 (1963).

155. W. Sundermeyer, Angew. Chem., 73, 763 (1961).

156. W. Sundermeyer, Z. Anorg. Allg. Chem., 314, 100 (1962).

157. J. Sugi and S. Saito, presented at Eur. Symp. Fresh Water Sea, Preprints Pap., 7, 93 (1967), Athens.

158. G. Tarbutton, E. P. Egan, Jr., and E. P. Frary, J. Amer. Chem. Soc., 63, 1782 (1941).

159. P. L. Timms, J. Chem. Soc., A, 2526, (1970).

160. H. W. Thompson and R. B. Temple, J. Chem. Soc., 1422 (1948).

161. T. E. Thorpe, J. Chem. Soc., 55, 759 (1889).

162. T. E. Thorpe and J. W. Rodger, J. Chem. Soc., 53, 766 (1888).

163. C. W. Tullock, Canad. Pat. No. 603,293, (1960).

164. C. W. Tullock, U. S. Pat. No. 2,928,720, (1960).

165. C. W. Tullock and D. D. Coffman, J. Org. Chem., 25, 2016 (1960).

166. C. A. Udovich, Ph.D. Dissertation, Florida State University, Tallahassee, Florida, 1969.

167. C. A. Udovich and R. J. Clark, J. Organometal. Chem., 36, 355 (1972).

168. J. R. Van Wazer, Phosphorus and its Compounds, Vol. I., Interscience Publishers, New York, 1958.

169. H. Valdsaar, Dissertation Abstracts, 22, 2579 (1962).

170. S. A. Voznesenski and L. M. Dubnikov, Zh. Obshch. Chim., 11, 507 (1941).

171. U. Wannagat and J. Rademachers, Z. Anorg. Allg. Chem., 289, 66 (1957).

172. J. D. Warren, M. A. Busch and R. J. Clark, Inorg. Chem., 11, (1972).

173. H. L. Welsh, M. F. Crawford and G. D. Scott, J. Chem. Phys., 16, 97 (1948).

174. K. Wiechert, Z. Anorg. Allg. Chem., 261, 310 (1950).

175. C. J. Wilkins, J. Chem. Soc., 2726 (1951).

176. G. Wilkinson, J. Amer. Chem. Soc., 73, 5501 (1951).

177. A. A. Williams, Inorganic Synthesis, 5, T. Moeller

178. J. N. Wilson, J. Amer. Chem. Soc., 80, 1338 (1958).

179. T. Wittstruck, W. Brey, Jr., A. M. Buswell and W. H. Rodebush, J. Chem. Eng. Data, 6, 343 (1961).

180. L. A. Woodward and J. R. Hall, Spectrochim. Acta, 16, 654 (1960).

181. A. A. Woolf, J. Chem. Soc., 1053 (1950).

182. A. A. Woolf, J. Chem. Soc., 279 (1955).