THERMODYNAMIC ASPECTS OF PHOSPHORUS COMPOUNDS WITH PARTICULAR REFERENCE TO THOSE CONTAINING THE PHOSPHORUS-PHOSPHORUS BOND.

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ABSTRACT

The enthalpies of sublimation for triiodophosphine and diphosphorus tetraiodide have been determined via an effusion manometric technique as 15.2 ± 0.9 (63.6 ± 3.8 KJ. mole^{-1}) and 16.7 ± 0.5 kcal mole^{-1} (69.9 ± 2.1 KJ. mole^{-1}) respectively. Incorporating these values in thermodynamic cycles along with ancillary literature data has resulted in a phosphorus-phosphorus bond energy in diphosphorus tetraiodide of 62 kcal mole^{-1} (259 KJ. mole^{-1}).

Mass spectrometric measurement of the appearance potentials for triiodophosphine and diphosphorus tetraiodide gave 11.9 ± 0.15 and 12.8 ± 0.15 eV respectively. These data in combination with known ionization potentials give 73 ± 6 kcal mole^{-1} (305 ± 25 KJ. mole^{-1}) for the bond dissociation energy of the phosphorus-phosphorus bond in diphosphorus tetraiodide. Cracking patterns for some mononuclear adducts of the type X_3PBX_3 (X = Br or I) are reported.

Reproducible synthetic routes for pentaphenylcyclopentaphosphine and polymeric phenylphosphine have been established. Thermochemical investigations have been made for the pentameric and polymeric phosphobenzenes by reaction-solution calorimetry and thermal analysis techniques.

The standard heat of formation of tricyanophosphine (crystal) is derived via thermochemical measurements as 133.6 ± 0.4 kcal mole^{-1} (559.0 ± 1.7 KJ. mole^{-1}) at 25°C.

The enthalpy of complexing of diphosphorus tetraiodide-boron tribromide (1:2) adduct from diphosphorus tetraiodide and boron tribromide in carbon disulphide has been measured as -2.13 ± 0.29 kcal mole^{-1} (-8.91 ± 1.21 KJ. mole^{-1}) and the standard heat of formation of this molecular adduct is derived as -144.0 ± 1.6 kcal mole^{-1} (602.5 ± 6.7 KJ. mole^{-1}). The enthalpy of hydrolysis

of pentabromophosphorane-boron tribromide is also recorded from which the standard heat of formation is found to be -142.0 ± 1.3 kcal $mole^{-1}$ (-594.1 ± 5.4 KJ. $mole^{-1}$).

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Dedicated to the inspiration of
the late Hon. Lady Hanifa Bai

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SECTION-I. INTRODUCTION

CHAPTER ONE:

INTRODUCTION

(1) Classification and Nomenclature of Phosphorus Compounds

The type of phosphorus compounds synthesised or used in the present investigation may be classified as

(i) cyclic phosphorus-phosphorus bonded compounds
(ii) acyclic phosphorus-phosphorus bonded compounds
(iii) mononuclear phosphorus compounds
(iv) molecular adduct of phosphorus compounds
and (v) pseudohalides of phosphorus

The naming of the cyclic structures may be treated as an extension of the system followed by Cowley[1] while that for the acyclic compounds, molecular adducts, and pseudohalides is due to the Chemical Society[2]. Some examples of the nomenclature are as follows.

Phosphorus-Phosphorus Bonded Compounds

(cyclic and acyclic in which phosphorus atom is in trivalent state)

Pentaphenylcyclopentaphosphine	$(C_6H_5P)_5$
Hexaphenylcyclohexaphosphine	$(C_6H_5P)_6$
Polymeric phenylphosphine	$(C_6H_5P)_n$
Diphosphorus tetraiodide	P_2I_4

Phosphorus (III) Compounds and Phosphorus (III) Pseudohalides

Phenylphosphine	$C_6H_5PH_2$
Phenyldibromophosphine	$C_6H_5PBr_2$
Tricyanophosphine	$P(CN)_3$
Tri(isocyanato)phosphine	$P(NCO)_3$
Tri(isocyano)phosphine	$P(NC)_3$
Tri(thiocyanato)phosphine	$P(SCN)_3$
Tri(fulminato)phosphine	$P(ONC)_3$

Phosphorus (V) Compounds

Phenyltetrachlorophosphorane	$C_6H_5PCl_4$
Phenyltetrabromophosphorane	$C_6H_5PBr_4$
Phosphoric oxide	P_4O_{10}

Molecular Adducts of Phosphorus

Diphosphorus tetraiodide- Boron tribromide (1:2) adduct	$P_2I_4 2BBr_3$
Tribromophosphine- Boron triiodide (1:1) adduct	PBr_3BI_3
Triiodophosphine- Boron tribromide (1:1) adduct	PI_3BBr_3
Pentabromophosphorane- Boron tribromide (1:1) adduct	PBr_5BBr_3

Organo-substituted Oxy-acids of Phosphorus

Phenylphosphonous acid	$C_6H_5PO_2H_2$
Phenylphosphonic acid	$C_6H_5PO_3H_2$
Phenylphosphinic acid	$(C_6H_5)_2PO_2H$

(See Appendix six for full details of the classification)

(2) Some Aspects of Chemical Thermodynamics

A quantitative knowledge of energy changes is essential not only for a complete understanding of known reactions but also to make more predictions (see Appendix five p. 240) about still untried reactions. It is changes in the electronic energy in the ground state which commonly dominate the total energy change for a chemical reaction. The general term "bond energy"[3-13] is a composite term. Logically, bond energy should be defined in a manner which must be understandable and experimentally derivable. In thermodynamics bond energy is defined[3] at 0°K in the absence of zero-point vibrational energy. Values derived at 298°K include zero-point contribution in addition to rotational, translational and further vibrational components. However, for the majority of polyatomic molecules it is not possible to evaluate these contributions so it is conventional to express bond energies at 298°K.

Recently bond energies data for bonds[14-20] in like atoms have been classified according to the position of the atoms in the periodic table.[3,21] The values in such tables are derived either from a theoretical basis or are practically determined via thermochemical measurements[3,12,22] or both.[14,21,23,24,25] The present position of such tables indicates the necessity for ascertaining more experimental values and for revising those estimated previously. In the present investigation the bond energy for the phosphorus-phosphorus bond is determined via thermochemical measurements.

In practice many thermochemical[3,12,26,27,28] values are obtained from combustion,[29] reaction-solution calorimetry,[12,29] equilibrium measurements[26,30,31,32] etc. which are prerequisite for deriving thermodynamic data. The useful quantity most commonly derived is standard heat of formation ($\Delta H^{o}f$) of the compound under standard conditions of temperature and pressure. Usually it is difficult to obtain heats of formation directly from the constituent elements. Thus the normal procedure is to measure the enthalpy change of a reaction of the compound which yields products of known heat content. For any reaction to be studied thermodynamically it is essential that its stoichiometry be known exactly.[33] The thermochemical values derived in the present work are obtained from constant temperature environment and adiabatic calorimetry operated at atmospheric pressure and at 25°C. The enthalpy change obtained for any general reaction may be expressed as

$$\Delta H = \Sigma \Delta H^o f \text{ (products)} - \Sigma \Delta H^o f \text{ (reactant)}$$

and when the products and reactants are in their standard states (the most stable form at 1 atm. and 25°C), then

$$\Delta H = \Delta H^o$$

For calculating the bond energy and average bond energy the most essential quantities needed are standard heat of formation, $\Delta H^o f$; sublimation enthalpy, $\Delta H(c \rightarrow g)$; and enthalpy of atomisation, ΔH atom. The latent heat of sublimation mentioned above is often estimated[32] in the absence of the experimental values. The sublimation enthalpy is always the most difficultly-accessible function for the determination of bond energies in compounds whose standard states are crystalline and which melt with decomposition. In this investigation, the sublimation enthalpy for triiodophosphine and diphosphorus tetraiodide have been determined via effusion manometry.

In common practice, therefore, the measurements of enthalpy change of reaction are achieved by direct or indirect methods. The direct[34] method employs calorimetry (combustion or reaction-solution) while the indirect[34] method make use of the slope of a graph of either log K vs. T^{-1} or log p vs. T^{-1} to obtain ΔH^o (as in effusion manometry)

$$\frac{\partial (\ln p)}{\partial T} = \frac{\Delta H^o}{RT^2}$$

where, ΔH = enthalpy change, p = pressure, T = absolute temperature, R = gas constant.

Calorimetry as a direct method is regarded as superior[35] to all indirect methods. Thermochemical investigations made by this technique cover a wide range of reactions.[3,29,35,36] They include hydrolysis, aminolysis, complexing, partial oxidation and aqueous oxidation with bromine. Thermochemical data obtained from reaction-solution calorimetry usually compare favourably with the same data derived from combustion calorimetry. As an illustration Head[37] obtained $\Delta H^o f$ ($H_3PO_4.40\ H_2O$) from combustion calorimetry using a rotating bomb calorimeter as -309.34 ± 0.4 kcal mole^{-1} (by combustion of white phosphorus in a "wet" bomb to get a final thermodynamic state $H_3PO_4.40\ H_2O$). From reaction-solution calorimetry Birley and Skinner[38] determined $\Delta H^o f$ ($H_3PO_4.100\ H_2O$) = -309.90 ± 0.35 kcal mole^{-1} using the following reaction.

$$PCl_5(c) + (n+4)\ H_2O(l) = (H_3PO_4 + 5HCl)\ nH_2O\ (soln.)$$

The phosphorus compounds studied here, are from reaction-solution calorimetry which include some of the phosphorus-phosphorus bonded compounds, phosphorus (III) and phosphorus (III) pseudohalides, phosphorus (V) compounds and the molecular adducts of type $P_2X_4 2BY_3$ and PX_5BY_3 (where X and Y are halogen). The reactions investigated were ring degradation with bromine, oxidative hydrolysis, aqueous oxidation with bromine and complexing.

Bond Dissociation Energy - One method[4,25,39,40,41] by which this quantity may be determined is mass spectrometry. The essential requirement is the accurate measurement of appearance potentials and ionization potentials. In appearance potential measurements it is probable that some excess kinetic energy is imparted to the fragments and results obtained must be treated as upper limits[25]. The investigations made here are concerned with appearance potential measurement for phosphorus iodides. Incorporation of the relevant literature ionization potentials has resulted in the calculations of the bond dissociation energies D_{I_2P-I} and $D_{I_2P-PI_2}$. The probable cracking patterns were also investigated in some phosphorus (III) and boron (III) compounds and in molecular adducts of the type X_3PBY_3 (where X, Y are halogen).

Thermal Analysis - This is one of the most rapid and useful techniques[42] for investigating phase equilibria,[43,44] decompositional[45,46] analysis and for the determination of enthalpies of fusion, dissociation and association energies, purity[47,48] and percentage crystallinity.[49] Thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) have been adapted to study diphosphorus tetraiodide, pentaphenylcyclopentaphosphine, hexaphenylcyclohexaphosphine, polymeric phenylphosphine and diphosphorus tetraiodide-boron tribromide (1:2 adduct). All of these compounds were manipulated in an inert atmosphere of nitrogen.

The aims of these investigations were:

(i) to ascertain if diphosphorus tetraiodide decomposed prior to the melting point (TGA)

(ii) to determine the heat of fusion, precise melting point, and purity of pentaphenylcyclopentaphosphine (DTA and DSC)

(iii) to investigate the inter-conversion of the phosphobenzenes pentaphenylcyclopentaphosphine, hexaphenylcyclohexaphosphine and polymeric phenylphosphine (DSC) and

(iv) to estimate quantitatively the relative dissociation energies in removing each of the boron tribromide molecules from diphosphorus tetraiodide boron tribromide (1:2 adduct) (TGA and DTA).

(3) Chemistry and Energetic Aspects of Phosphorus Compounds

Phosphorus Chemistry began three centuries ago with the discovery of the element, then called "light bearer"[50], and since then the major interest in synthesis has been confined to mononuclear phosphorus compounds and their derivatives. Relatively new classes of compounds have emerged within the last two decades (see pp.14,24). This may be attributed to considerable interest in mechanistic,[51-59] synthetic,[1,59-67] structural[59,63,66,68-72] and energetic[7,8,32,37,59,73-76] aspects of phosphorus-phosphorus bonded compounds in particular, phosphorus compounds and elemental phosphorus in general.

For convenience, the chemistry and energetic aspects of the compounds synthesised in this investigation will be described under the following headings (i) Phosphorus-Phosphorus Bonded Compounds (cyclic and acyclic)

(ii) Phosphorus (III) Pseudohalides and Phosphorus (III) Compounds

(iii) Phosphorus (V) Compounds

(iv) Molecular Adducts

(i) Phosphorus-Phosphorus Bonded Compounds (cyclic and acyclic)

(a) Phosphobenzene

There is considerable current interest in compounds containing the phosphorus-phosphorus bond. It is obvious from recent publications and reviews[1,61,62,63,64,66] on phosphorus-phosphorus bonded compounds that physical data for these compounds are scarce. Although most synthetic procedures are quite well-established, there seem to be unusual difficulties associated with the preparation of phosphobenzene, mainly due to interconversion in solution. This either results in pentaphenylcyclopentaphosphine, hexaphenylcyclohexaphosphine, or the so called polymeric phenylphosphine. There is no definite reproducible route for synthesising hexaphenylcyclohexaphosphine or polymeric phenylphosphine. The pentaphenylcyclopentaphosphine may be readily prepared by the procedure of Fraxier[77] et al, then reported as the tetramer. The compound is now well-characterised by Daly[78,79] as pentamer and X-ray analysis data are compared in the present investigation (see Appendix four).

Phosphobenzene was first prepared by Köhler and Michaelis[80] in the year 1817 from phenylphosphine and phenyldichlorophosphine. The resulting pale yellow crystalline mass (m.pt. 149-150°C) was assigned a similar formula to azobenzene and called phosphobenzene $C_6H_5P = PC_6H_5$. On further investigation, the reactivities towards oxygen, chlorine, hydrogen chloride and water were established. Reaction of phosphobenzene with hydrochloric acid decomposed the material into phenylphosphine and phenyldichlorophosphine. Similarly, reaction with chlorine produced phenyldichlorophosphine.

However, no peculiar emphasis was placed upon the isolation of phosphobenzene and this interesting field remained dormant for sixty-five years. In the year 1952, studies conducted by Erlenmeyer[81] et al. revealed the complex nature of this compound. The preparation was essentially the same as Michaelis and Kohler but the resulting material obtained was quite different. This substance was a white crystalline solid with m.pt. 193°C in a sealed tube (compared to 149-150°C). The empirical formula assigned to the new compound on the basis of microanalysis for carbon, hydrogen, and phosphorus, was $C_{12}H_{10}P_2$. The molecular weight by the camphor technique was 198, which corresponds approximately to $(C_6H_5)_2P$. It was also suggested that the product made by Michaelis and Kohler was grossly impure. Reesor and Wright,[82] in 1957, repeated exactly the work of Erlenmeyer et al. with the six-fold increase in the size of the experiment a different material was obtained. This material was also different from that of any of the other previous workers.

The melting point of this substance was 252-256°C, finally becoming clear at 278°, then remelting at 148°C. It was also found that Erlenmeyer's compound (m.pt. 193°C), remelted at 148°C. This was followed by the determination of the molecular weight of these compounds by the isopiestic method in carbon disulphide. The results obtained are as follows:

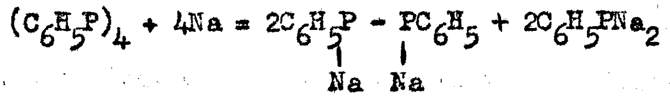
M.pt. (°C)	Mol.wt.
154-156	206 (calc. 216)
193	402 (calc. 432)
252-256 onto 278	Polymeric

The high melting point substance (m.pt. 252>) was also found to be insoluble in most of the solvents.

In 1957, Mahler and Burg[83], working on $(F_3CP)_4$, postulated that phosphobenzene had a tetrameric structure. This was supported by Kuchen and Buchwald[84] from the results of molecular weight studies. Accordingly the structure of the substance melting at 154-156°C was assigned the formula $(C_6H_5P)_4$ i.e. tetraphenylcyclotetraphosphine. The chemistry of this compound was demonstrated in terms of oxidation, bromination and adduct formation etc. Some of the interesting reactions were:

(i) $(C_6H_5P)_4 + 4Br_2 = 4C_6H_5PBr_2$

(ii) $(C_6H_5P)_4 + 4O_2 + 4H_2O = 4C_6H_5PO(OH)_2$

(iii) 

$$(C_6H_5P)_4 + 4Na = 2C_6H_5\underset{\substack{|\\ Na}}{P} - \underset{\substack{|\\ Na}}{P}C_6H_5 + 2C_6H_5PNa_2$$

The initial reaction in (iii) with sodium was shown to retain the phosphorus-phosphorus bond. Further addition of sodium completely destroyed the P-P linkage. The resulting compound was a mononuclear phosphorus adduct. It may be recalled at this point that Reesor and Wright did not observe any monoadduct.

In 1963, Henderson[62] et al. undertook a detailed survey of the cyclopolyphosphines and proposed new approaches for synthesising and characterizing these compounds. According to Henderson phosphobenzene was treated as a group of compounds and classified as

Form	M.pt.(°C)	
(A)	148-152	Tetraphenylcyclotetraphosphine
(B)	195-199	
(C)	270-283	Polymeric Phenylphosphine
(D)	260-285	

The methods of synthesis for form (A) were based on (i) the reaction of phenylphosphine and phenyldichlorophosphine in ether (ii) reduction of phenyldichlorophosphine with magnesium in ether or tetrahydrofuran and (iii) reduction of phenyldichlorophosphine with lithium aluminium hydride. The synthesis for form (B) was via phenylphosphine and phenyldichlorophosphine in benzene and the same procedure was followed for form (C) and form (D) except that cyclohexane was used as solvent.

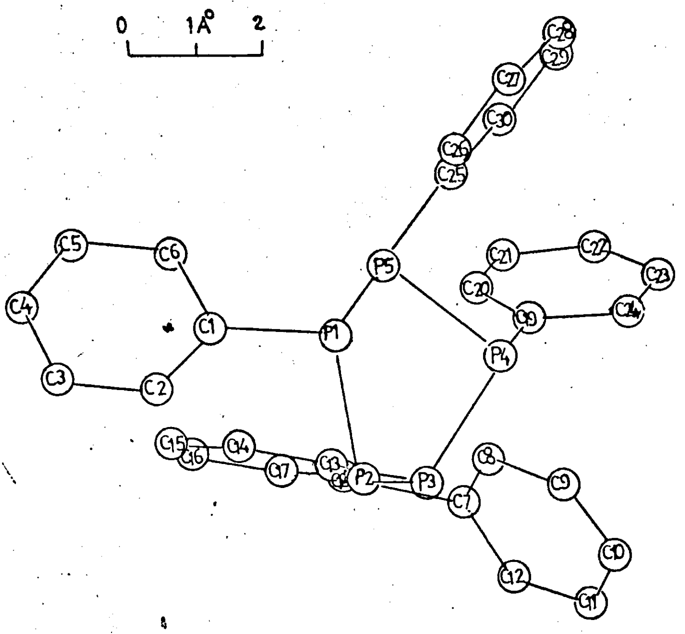
It can be seen that essentially the method for preparation of all three forms is more or less the same as the previous syntheses. Detailed investigations of physical properties of phosphobenzene by various techniques have appeared in the literature. These include for form (A) and (B) (i) the determination of the molecular weight by isopiestic, cryoscopic and ebullioscopic methods in a variety of solvents (ii) mass spectrometric analyses with heated inlet system at 200°C (iii) ultraviolet spectroscopy (iv) nuclear magnetic resonance for hydrogen and phosphorus and (v) infra-red (also for form (C) and (D)) and Raman spectroscopy (see for comparison of these with the present investigations in Appendix three). From these studies it has been concluded that both form (A) and (B) are tetraphenylcyclotetraphosphine, although both differ in structure in solution and solid phase.

At this time (1963), the problem of (i) explicit synthetic routes (ii) the mechanism of interconversion in solution and (iii) molecular structure, remained equivocal.

During 1964, Fraxier[77] et al. developed a method of synthesis for tetraphenylcyclotetraphosphine m.pt. 147-150°C (now adapted in the present investigation for pentaphenylcyclopentaphosphine, see chapter two: Synthesis) based on the reaction of phenyldichlorophosphine and tributylphosphine. The resulting compound was characterised by microanalysis and infra-red spectra and was identical with that of Kuchen and Buchwald.[84]

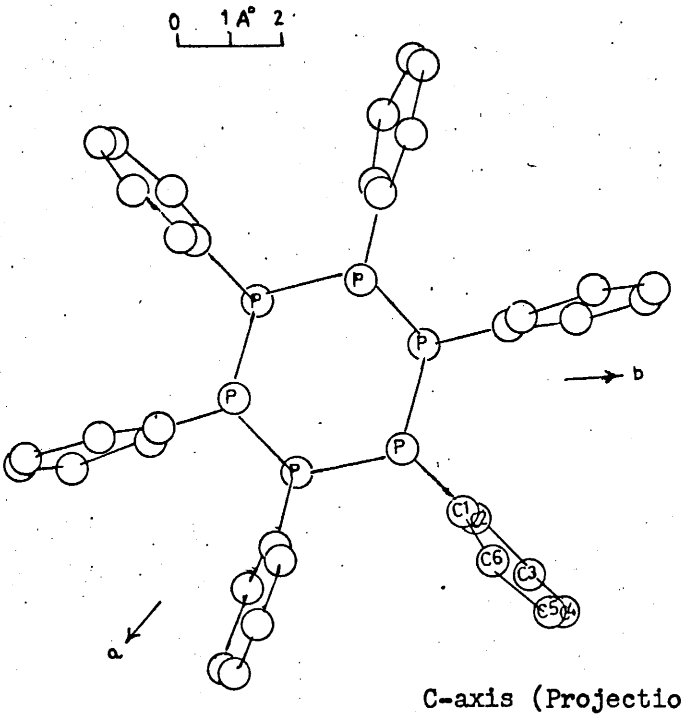
In 1964 onwards, Daly[78,79] produced X-ray crystallographic evidence on form (A) m.pt. 149-150° which was found to be monoclinic and existing as pentaphenylcyclopentaphosphine. In this form, the phosphorus atoms form an equilateral pentagon (see diagram for structures on pp.25,27). The crystalline phosphobenzene form (B) m.pt. 190°C (193°C) is polymorphic. There are at least four crystal modifications[85] known, consisting of monoclinic, triclinic, trigonal and hexagonal types, (see diagram for structure of trigonal modification on p.26). All have the structure hexaphenylcyclohexaphosphine.

The crystalline phosphobenzene forms (C) and (D) (melting range 260-285°C, the so-called polymeric forms) give the same[86] X-ray diffraction pattern. The structures of these are not yet known, nor their molecular weight. There also exists no reproducible synthetic route for these compounds.



(a) perpendicular to paper.

Fig. Crystal Structure of Pentaphenylcyclopentaphosphine.
(after J.J. Daly [78])



C-axis (Projection of the molecule)

Fig. Crystal Structure of Hexaphenylcyclohexaphosphine (Trigonal) (after J.J. Daly)[79]

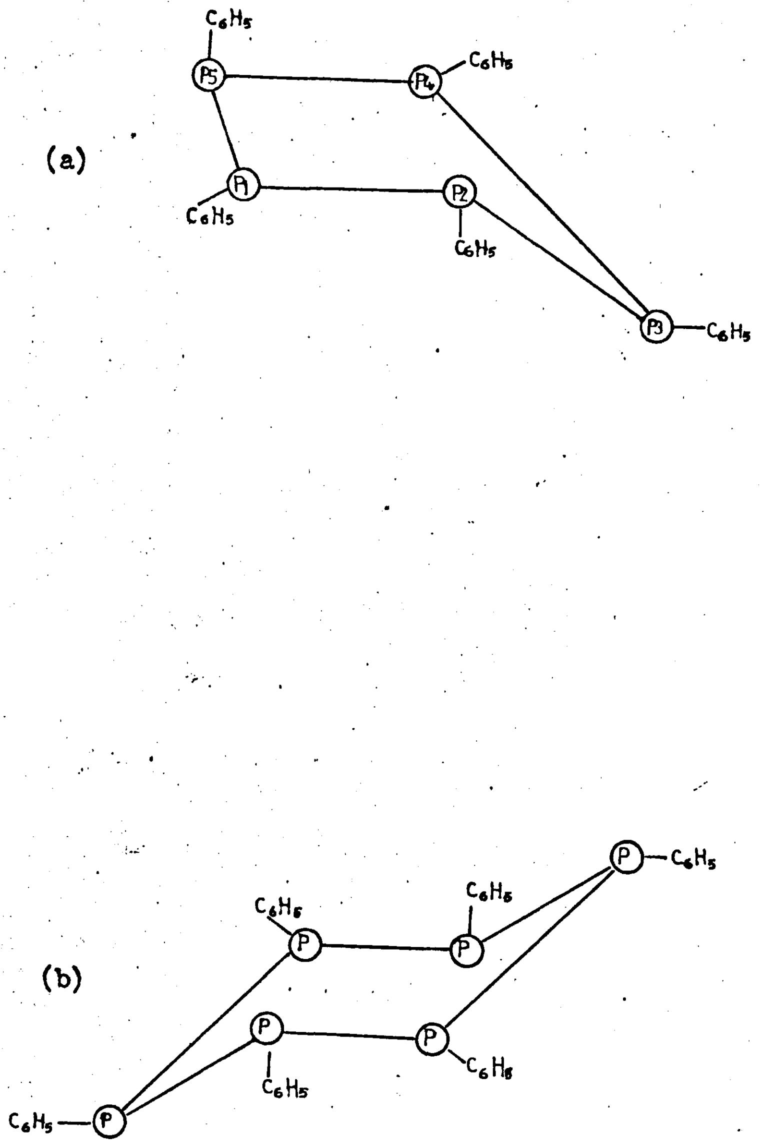
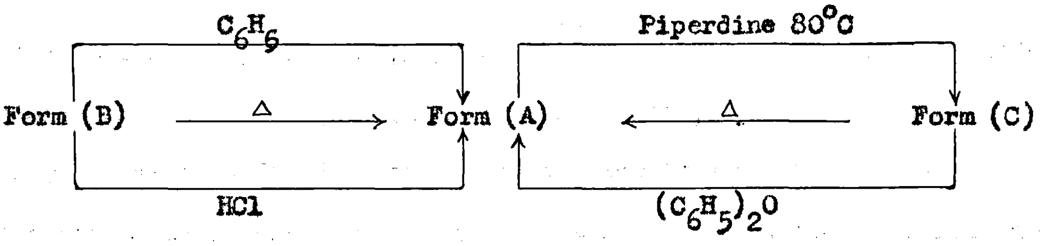


Fig. Molecular Stereochemistry (after L. Maier[63]).
(a) Pentaphenylcyclopentaphosphine.
(b) Hexaphenylcyclohexaphosphine.

The problem in devising direct synthetic routes for all known forms of phosphobenzene was investigated by Maier[63,85] in 1966. A new method of synthesis for pentaphenylcyclopentaphosphine (form (A)) was devised which was based on the following reaction.

$$5\,C_6H_5PH_2 + 5\,C_6H_5P(N(CH_3)_2)_2 = 2(C_6H_5P)_5 + 10\,HN(CH_3)_2$$

In another attempt to find a reproducible route for the synthesis of hexaphenylcyclohexaphosphine (form (B)), Henderson's work was repeated in a modified way. Limited success was achieved when the reaction of phenylphosphine and phenyldichlorophosphine was carried out in triethylamine. Inexplicably, however, on numerous occasions this reaction produced the common form (A). After detailed, but inconclusive studies, Maier suggested a probable interconversion scheme, which is as follows.



The exact conditions for these changes are not yet probably understood. These changes, in the solid phase, have been studied as part of this work, (see Chapter seven: Thermal Analysis Results). The X-ray powder pattern for each form has been studied by Maier[63] and his results are compared with similar data in this work. Currently, there are no thermodynamic data for the phosphobenzene.

In conclusion, it appears that phosphobenzene is becoming a most useful precursor for the synthesis of phosphorus-phosphorus bonded compounds.

(b) Phosphorus Iodide

Phosphorus iodide (probably triiodide) was first synthesised via combination of the elements by Gay-Lussac[87] in 1813. Diphosphorus tetraiodide was synthesised by Hoffmann[88] (1857) via the reaction

$$8PH_3 + 5I_2 = P_2I_4 + 6PH_4I$$

In 1900, Michaelis and Pitsch[89] successfully prepared diphosphorus tetraiodide by reacting elemental phosphorus and iodine in the stoichiometric quantities in carbon disulphide

$$2P(w) + 2I_2 = P_2I_4$$

This reaction demonstrated that partial retention of a P-P linkage was possible.

In 1925 and 1927, Traxler and Germann[91] undertook a detailed investigation of these syntheses. It was ascertained that free sulphur in the carbon disulphide interfered in the main reaction to give $P_4S_3I_2$. A method of purification was suggested which was adopted with minor modifications in the present work (see Chapter two: purification).

According to Baudler and Fricke[92] (in 1963) controlled oxidation of diphosphorus tetraiodide resulted in a polymer with the following composition.

$$7P_2I_4 + 6O_2 \longrightarrow 2/n\,(P_3I_2O_6)_n + 8PI_3$$

This study also indicated that dissolved oxygen in carbon disulphide could be a source of interference in the synthesis of iodides. Hence scrupulously dry and pure solvent is essential. Also handling should be carried out in a dry inert atmosphere, e.g. nitrogen.

The structural aspects of iodides, especially triiodophosphine and diphosphorus tetraiodide, have been studied by several techniques,[55] such as vibrational spectroscopy (infra-red,[93,94] Raman[94]), by ^{31}P n.m.r.[57,93] and by X-ray crystallography[95,96] . Results for triiodophosphine indicate that the molecule is pyramidal[65] in shape. The interatomic distance[96] between P-I is 2.46°A with a bonding angle I-P-I of 100° and symmetry C_3v. The van der Waal radius for iodine is 2.15°A. The diphosphorus tetraiodide molecule has the "trans" conformation[93,94] in the solid and also in carbon disulphide, dichloromethane or benzene (C_2h). The P-P distance[95] is 2.21°A, the P-I bond length is 2.475°A, the I-P-I bonding angle is 102°18', and I-P-P is 93°58' and 93°56'.

A ^{31}P n.m.r. study, by Carroll and Carter[57] in 1967, was conducted for the formation of diphosphorus tetraiodide from the reaction of elemental phosphorus and iodine. The results indicate (i) all the phosphorus-phosphorus bonds are broken when the reaction is performed in carbon disulphide or carbon tetrachloride at 25°C. Evidence is presented that diphosphorus tetraiodide is formed via triiodophosphine

$$\tfrac{1}{2} P_4 + 3I_2 \longrightarrow 2PI_3 \qquad \text{(fast)}$$
$$2PI_3 + \tfrac{1}{4}P_4 \longrightarrow \tfrac{3}{2} P_2I_4 \qquad \text{(slow)}$$

(ii) that the phosphorus/iodine system is very labile and there exist equilibria in solution of the type:

$$\tfrac{3}{2} P_2I_4 \rightleftharpoons 2PI_3 + \tfrac{1}{4} P_4$$

The existence of this equilibrium is supported also by the fact that identical U.V. spectra are obtained from solutions of triiodophosphine and diphosphorus tetraiodide in cyclohexane. Evidence is also presented for the existence of the equilibria such as

$$P_2I_4 + I_2 \rightleftharpoons 2PI_3$$

This equilibrium lies very much on the side of triiodophosphine.

A possible disproportionation reaction suggested by Cowley and Cohen[97] is

$$P_2I_4 \longrightarrow PI_3 + \frac{1}{n}(PI)_n$$

This results in the formation of a phosphorus iodide polymer along with triiodophosphine. The structure, molecular weight and composition are unknown.

Very recently (1970) Kennedy and Sinclair[55] have investigated the photochemical decomposition of cyclohexane and hexane solutions of triiodophosphine and diphosphorus tetraiodide. It has been suggested that disproportionation occurs with the formation of polymer along with triiodophosphine.

$$P_2I_4 \longrightarrow 1.17\ PI_3 + \frac{1}{6n}(P_5I_3)_n$$

This reaction indicates the stoichiometry of the polymer but the molecular weight is unknown. A simple linear structure of this polymer is proposed.

Recently (1967) Payne[65] has reviewed the chemistry of phosphorus halides. It is clear that considerable interest is developed in the chemical properties of diphosphorus tetraiodide. The hydrolysis products have not yet been quantitatively evaluated due to the complex nature of reaction. According to Wiersman and Sandoval[98] alkaline hydrolysis of diphosphorus tetraiodide produces diphosphine, phosphorus acid and hypophosphorus acid. Similar products are also formed by acid hydrolysis along with unknown mixture of oxyacids.

The hydrolysis of triiodophosphine in hydrochloric acid (2N) and in water is shown[99,100] to yield quantitatively phosphorus acid and corresponding acid. The reaction is expressed as

$$PI_3 + 3H_2O = H_3PO_3 + 3HI$$

The addition reaction of triiodophosphine with boron tribromide in carbon disulphide has been first reported by Tarible[101] in 1901. The resulting adduct was assigned the formula $P_2I_4 2BBr_3$ after elemental analysis. The modified syntheses by Cowley and Cohen[97] has shown that the reaction of boron tribromide with (i) triiodophosphine proceeds according to the following equation in carbon disulphide as

$$PI_3 + BBr_3 = PI_3BBr_3$$

and (ii) with diphosphorous tetraiodide as

$$P_2I_4 + 2BBr_3 = P_2I_4 2BBr_3$$

The crystalline structures of these adducts have been elucidated by X-ray diffraction pattern and compared with those of the parent iodides. The other physical techniques used for characterization are ^{11}B n.m.r., and I.R. The same method of adduct synthesis is adopted in the present work.

The reaction of sulphur[102] with triiodophosphine is additive.

$$PI_3 + S = SPI_3$$

Although the existence and stability[91,103] of the compounds like P_3I_4 and P_4I[103] have been claimed almost a century ago, there are no thermodynamic data to substantiate these claims. The first reported values for the phosphorus iodides was by Ogier[89] in 1881. Accordingly ΔH^of PI_3 is

-10.9 kcal mole^{-1}, ΔH sol. PI_3 is 3.3 kcal mole^{-1} and ΔH sol. P_2I_4 is -5.0 kcal mole (in solvent CS_2). The reaction used for the derivation of ΔH^of was the synthesis from the elements. Very recently (1969) detailed thermochemical studies on phosphorus iodides[104] system have revealed considerable difference in ΔH^of and ΔH sol. The ΔH^of PI_3 is -14.7 kcal mole^{-1}, and ΔH^of P_2I_4 is -27.03 kcal mole^{-1}. The results have been derived from reaction-solution calorimetry, and the reactions utilized are well-characterized. These reactions are

$$P_2I_4 + I_2 = 2PI_3$$
$$PI_3 + 3H_2O = H_3PO_3 + 3HI$$

Attempts have also been made to estimate the average bond energy $\bar{E}_{P-I}$ in triiodophosphine and the bond energy $E_{I_2P-PI_2}$ in the absence of experimental data for the heats of sublimation. According to Hartley[32] et al. (assuming $E_{P-I} = \bar{E}_{I_2P-I} = 44$ kcal mole^{-1}) a value of 67 kcal mole^{-1} for phosphorus-phosphorus bond in diphosphorus tetraiodide is derived, "using the questionable value for the heat of sublimation of P_2I_4 of 30 kcal/mole". This value was estimated by Rice[105] in 1940; (for experimentally derived values of latent heat of sublimation for triiodophosphine and diphosphorus tetraiodide, see Chapter nine: Effusion Manomeric Results). In conclusion, diphosphorus tetraiodide is the only so far known crystalline diphosphorus halide. Although little emphasised[60,65] as a synthetic precursor until now, certainly it is the simple and most useful P-P bonded compound for the study of thermodynamic functions.

(ii) Phosphorus (III) pseudohalides and Phosphorus (III) Compounds

Phosphorus (III) pseudohalides

There is considerable interest in the synthetic,[67,106-116] mechanistic,[99,117-120] structural,[120-125,133] and energetic[107,126,127] aspects of pseudohalides of phosphorus, in particular tricyanophosphine and tri(isocyanato)phosphine. Although some physical data,[67,107,114] for example vapour pressure measurements, Troutons constant, etc. have been described in the literature, there are no thermochemical measurements for tricyanophosphine and tri(isocyanato)phosphine.

Pseudohalides (or halogenoids), as a well-defined class of compounds, were first reported by Browne[128] et al. in 1923, although the first known pseudohalide (tricyanophosphine) was synthesised by Cendella[129] in 1835. Gall and Schuppen,[130] in 1930, described a method of preparation based on the following reaction.

$$PCl_3 + 3AgCN = P(CN)_3 + 3AgCl$$

The resulting solid material sublimed at 190°C. A modification of the above procedure was suggested by Staat and Morgan,[115] using solvents such as chloroform, carbon tetrachloride and benzene. In this method the trichlorophosphine was allowed to react with the suspension of silver cyanide. The reaction mixture was refluxed for a period of 18 to 20 hr. The excess solvent and trichlorophosphine were removed by vacuum distillation, followed by the sublimation of the residue. The sublimed material melted close to 200°C (a similar procedure was adopted in the present synthetic work).

Recently (1963) Maier[116] devised a new synthetic route for tricyanophosphine. The reaction was based on the exchange reaction of tribromophosphine with silver cyanide in methylcyanide.

$$PBr_3 + 3AgCN = P(CN)_3 + 3AgBr$$

The resulting material turned orange at 180-200°C and decomposed without melting.

The solubility[115] of tricyanophosphine has been shown to be low in solvents such as chloroform, carbon disulphide, trichlorophosphine and ether. The reactivity of this compound with moisture is described as being very high. The hydrolysis products are identified as hydrogen cyanide, phosphorous acid and yellow phosphorus-containing compounds. Recently (1963), Pollard[99] et al. quantitatively estimated the hydrolysis products of pseudohalides and halides in sodium hydroxide (5N) and hydrochloric acid (2N). A chromatographic technique was used for this estimation (see Appendix one for a similar hydrolysis using a potentiometric technique). It was found that in 2N HCl, phosphorus pseudohalides hydrolyse quantitatively to phosphorus acid and the corresponding hydrogen pseudohalide. In a basic hydrolysing medium, a mixture of lower phosphorus acids with phosphorus acid was obtained.

A review[67] on phosphorus isocyanates has recently appeared and describes synthetic, physical and chemical aspects of these compounds. An unusual feature is the reversible polymerization of tri(isocyanato)phosphine, which was the first isocyanate reported by Forbes and Anderson[114] in 1940. The synthesis is based on the exchange reaction of silver isocyanate and trichlorophosphine in benzene (a similar procedure is adopted in the present work).

$$PCl_3 + 3AgNCO = P(NCO)_3 + 3AgCl$$

Structural aspects of the tri(isocyanato)phosphine have been investigated by infra-red and P^{31} n.m.r. techniques.

An interesting feature[114] of the reversible polymerisation was demonstrated by supercooling, liquid tri(isocyanato)phosphine at -20°C. A white solid appeared which melted at -2°C (however a sample which had not been cooled remained unchanged for fourteen days). The resulting liquid was held for three days at ambient temperature and deposited a white polymeric material which remelted at 80°C. The white solid was found to be insoluble in benzene, ether, chloroform and carbon tetrachloride.

In 1950, Anderson[131] presented another synthetic route dealing with the exchange reaction between triiodophosphine and silver isocyanate in nitromethane.

$$PI_3 + 3AgNCO = P(NCO)_3 + 3AgI$$

The same reaction when conducted in benzene did not proceed. This was the first time that a solvent effect on isocyanate synthesis was noticed. Anderson[132] also investigated the following redistribution reaction

$$2ClP(NCO)_2 = Cl_2PNCO + P(NCO)_3$$

which was carried out upon distillation under normal pressure.

Thermal stability of substituted isocyanate follows the order

$$P(NCO)_3 < ClP(NCO)_2 < Cl_2PNCO$$

There are no thermodynamic data available to substantiate the thermal instability of these compounds. (See Chapter six for thermochemical measurements).

After detailed investigation of exchange reactions in various pseudohalides an empirical generalization was put forward by Anderson[131] for predicting the outcome of untried reactions. Accordingly, (i) exchange reactions are only possible when the atom to be replaced has a larger single-bond radius than the reactant atom (ii) molar volume is no criterion for exchange reaction and (iii) the strength of the corresponding isocyanic acid is also no criterion.

In 1959, Jenkins[110] et al successfully devised a synthetic route for the preparation of tri(isocyanato)phosphine. The reaction investigated was

$$3\ LiNCO + PCl_3 = P(NCO)_3 + 3\ LiCl$$

This reaction was surprising, as the corresponding sodium and potassium isocyanates, after numerous attempts under various reaction conditions, did not react. The reaction conditions, involving potassium isocyanate and trichlorophosphine, included solvents such as benzene, toluene, xylene, carbon tetrachloride, nitromethane, liquid sulphur dioxide, liquid antimony trichloride and a mixture of solvents. In order to accelerate the reaction, catalysts were used, e.g. cuprous chloride. Also, reaction in the gas phase was tried. None of these produced any recoverable amount of tri(isocyanato)phosphine.

According to Jenkins[110] et al., "The thermodynamic equation for the reaction of potassium isocyanate and phosphorus trichloride indicates that they should react more readily than silver isocyanate and phosphorus trichloride. Yet, this is not the case".

However, four years later (in 1963) Fielding[109] successfully prepared tri(isocyanato)phosphine using the reactants sodium or potassium isocyanate and trichlorophosphine in polar organic solvents such as dry methyl cyanide or mixed solvent pairs such as benzene and petroleum ether, acetone and benzene, acetone and toluene, benzene and nitromethane. The equation for the reaction is as follows

$$PCl_3 + 3MNCO = P(NCO)_3 + 3MCl \qquad (M = K,Na)$$

The yield from the above reaction for tri(isocyanato)phosphine is claimed to be 62 to 95%.

The physical and chemical properties have been reviewed by Derkatsch.[67]

Some of the interesting properties for tri(isocyanato)phosphine include (i) violent reaction with water, aqueous sulphuric acid, aqueous silver nitrate, aqueous acetic acid and acetaldehyde. Reaction is mild with ether, ethyl alcohol, methyl alcohol, dimethyl ketone(warm), alkali metals and iodine. Tri(isocyanato)phosphine dissolves without reaction in dimethyl ketone(cold), benzene, chloroform, phenol, nitrobenzene, and propionic acid. Recently Pollard[99] et al. reported hydrolysis in 5NNaOH and 2NHCl. The hydrolysis products are quantitatively determined by chromatographic techniques. (See Appendix one for a similar hydrolysis where the products are evaluated by a potentiometric technique.) It was found that in 2N HCl the hydrolysis produced quantitatively phosphorous acid and isocyanic acid. These have been also reported earlier by Forbes and Anderson.[114] In conclusion, synthesis of phosphorus-phosphorus bonded compounds (Noth[111] and Derkatsch[67])using pseudohalides as precursors has been reported.

Phosphorus (III) Compounds

Numerous compounds of this type are now known which include mono-bi-tri and polynuclear derivatives. Reviews concerning synthetic[59,60,65,108,134,135] structural[59,65,108,134] and energetic[32,59,108] aspects have appeared. The phosphorus (III) derivatives of interest to this work are phenyldibromophosphine, phenyldichlorophosphine and phenylphosphine. The syntheses[84,136-138] of phenyldibromophosphine are based on the following reactions.

(i) $2C_6H_5PCl_2 + LiAlH_4 = 2C_6H_5PH_2 + LiCl + AlCl_3$

$C_6H_5PH_2 + Br_2 = C_6H_5PBr_2 + H_2$

(ii) $C_6H_5PCl_2 + 2HBr$ (anhyd.) $= C_6H_5PBr_2 + 2HCl$

This reaction (ii) is conducted in tribromophosphine as solvent. (See Chapter two: Synthesis, for further details.)

(iii) $C_6H_5PCl_2 + PBr_3 \longrightarrow C_6H_5PBr_2 + (PBr_{3-n}Cl_n)$

$n = 1,2$

This reaction proceeds at 100-200°C and the compounds $PBr_{3-n}Cl_n$ are removed by continuous distillation. The resulting material, phenyldibromophosphine, has a b.pt. 124 to 126°C/11 mm.Hg.

Chemical and physical properties of phenyldibromophosphine of interest are:

(i) Hydrolysis: this yields quantitatively phenylphosphonous acid and hydrobromic acid.

$$C_6H_5PBr_2 + 2H_2O = C_6H_5PO_2H_2 + 2HBr$$

A thermochemical investigation[139] based on this reaction gave an estimate of the standard heat of formation of liquid phenyldibromophosphine as Ca. -8 kcal $mole^{-1}$ and for crystalline phenylphosphonous acid as -130 kcal $mole^{-1}$ Precise thermodynamic data for phenylphosphonous acid are lacking.

(ii) The reaction[137] with magnesium is reported (1963) to produce a cyclic compound, then called tetraphenylcyclotetraphosphine.

$$C_6H_5PBr_2 + Mg = \tfrac{1}{4}(C_6H_5P)_4 + MgBr_2$$

(iii) The reaction[140] with pentaphenylcyclopentaphosphine causes partial degradation of the ring.

$$C_6H_5PBr_2 + \frac{1}{5}(C_6H_5P)_5 = (C_6H_5)_2P_2Br_2$$

Similar partial or complete degradation reactions may proceed by altering the stoichiometry, e.g.

$$\frac{2}{5}(C_6H_5P)_5 + Br_2 = (C_6H_5)_2P_2Br_2 \qquad \text{(partial)}$$

$$\frac{1}{5}(C_6H_5P)_5 + Br_2 = C_6H_5PBr_2 \qquad \text{(complete)}$$

The latter reaction is quantitatively investigated in the present work by titrimetry (see Chapter Six: Thermochemical Results).

(iv) With lithium, phenyldibromophosphine reacts to produce a trinuclear phosphorus compound.

$$3C_6H_5PBr_2 + 6LiH = (C_6H_5)_3P_3H_2 + 6LiBr + 2H_2$$

(v) Phenyldibromophosphine reacts with mercury at 80°C under reflux, and the product in high yield is phosphobenzene.[60]

$$C_6H_5PBr_2 + 2nHg = (C_6H_5P)_n + nHg_2Br_2$$

The phosphobenzene produced in this reaction has a m.pt. of 151°C and therefore is presumably form (A).

Various methods of synthesising phenyldichlorophosphine have been described in the literature.[108,135] The synthesis reported in 1879 by Michaelis and Dittler[141] is now usually employed in a modified form. According to Henderson[142] et al. the modification is the slow and low-temperature (-50°C) transfer of primary phosphine onto carbonyl chloride dissolved in inert solvents such as methylene dichloride and carbon tetrachloride. On slow warming, reaction takes place.

$$RPH_2 + 2COCl_2 = RPCl_2 + 2CO + 2HCl$$

$$(R = C_6H_5, C_4H_9, C_6H_{11}, C_8H_{11})$$

Recently Maier[59] (1963) proposed a probable mechanism for this reaction.

$$\begin{array}{c} 4C_6H_5PH_2 + 4COCl_2 \longrightarrow (C_6H_5P)_4 + 4CO + 8HCl \\ \Big\downarrow + 4COCl_2 \\ 4C_6H_5PCl_2 + 4CO \end{array}$$

Phenyldichlorophosphine is of interest as a synthetic precursor for phosphorus-phosphorus bonded compounds:

(i) Reaction with primary phosphine produces a cyclic compound[61] e.g.

$$RPCl_2 + RPH_2 = 2/n\,(RP)_n + 2HCl$$
$$(R = \text{alkyl, aryl } (C_6H_5))$$

The reaction is carried in the absence of solvent or in the presence of benzene, ether, petroleum ether, toluene, cyclohexane etc.

(ii) Reaction with metals, such as lithium, sodium, magnesium, zinc in solvents like tetrahydrofuran, ether, benzene etc., produce cyclic phosphine.[61]

$$RPCl_2 + 2M = 1/n\,(RP)_n + 2MCl$$
$$(R = \text{alkyl, aryl } (C_6H_5))$$

Phenylphosphene is now most conveniently prepared by the method of Fluck and Binder.[143] The preparation is carried out in ether as solvent.

$$2C_6H_5PCl_2 + LiAlH_4 = 2C_6H_5PH_2 + LiCl + AlCl_3$$

These investigators suggest that an intermediate complex, $Li(H_3Al.PC_6H_5(Cl))$, is formed prior to the hydrolysis (see Chapter two: Synthesis, for detailed procedure).

Phosphorus (V) Compounds

Many compounds of general formula PX_5, $PX_n\,Y_{5-n}$ have been described in the literature which covers synthetic,[65,108,134] structural,[65,108,134] mechanistic[51] and energetic[32,65,134] aspects. The substituted compounds are usually alkyl or aryl. Of interest here are phenyltetrachlorophosphorane and phenyltetrabromophosphorane.

The methods of syntheses[135] for phenyltetrachlorophosphorane are based on the addition reaction of chlorine to phenyldichlorophosphine. A convenient method is described by Herring and Douglas[144] (see Chapter two: Synthesis: for experimental details).

$$C_6H_5PCl_2 + Cl_2 = C_6H_5PCl_4$$

Other solvents have been proposed[145] for this reaction, while the method of Michalis[146] uses no solvent at all.

Phenyltetrachlorophosphorane[147] on heating decomposes into chlorine and phenyldichlorophosphine.

$$C_6H_5PCl_4 \longrightarrow C_6H_5PCl_2 + Cl_2$$

On heating in a pressure tube at 180°C trichlorophosphine and chlorobenzene are formed[147].

$$C_6H_5PCl_4 = C_6H_5Cl + PCl_3$$

Phenyltetrachlorophosphorane is hygroscopic and reacts vigorously with water forming phenylphosphonic acid.

$$C_6H_5PCl_4 + 3H_2O = C_6H_5PO_3H_2 + 4HCl$$

Phenyltetrabromophosphorane[147] is synthesised by the addition reaction of bromine to phenyldibromophosphine in the absence of solvent.

$$C_6H_5PBr_2 + Br_2 = C_6H_5PBr_4$$

A similar preparation in the presence of carbon tetrachloride was performed in this investigation (see Chapter two: Synthesis).

Phenyltetrabromophosphorane is hygroscopic and reacts with water to produce phenylphosphonic acid (see Chapter six: Thermochemical Results).

$$C_6H_5PBr_4 + 3H_2O = C_6H_5PO_3H_2 + 4HBr$$

Currently there are no thermochemical measurements available for phenyltetrachlorophosphorane and phenyltetrabromophosphorane.

(V) Molecular Adducts

The tendency of phosphorus halides to form molecular adduct, especially with boron halides, was noted by Tarible[101] seventy years ago. Since 1960 there has been considerable interest in such adducts. The literature includes synthetic,[72,97,148] structural,[72,97,148] and energetic[72,148,150] aspects. The molecular adducts synthesised include mon-, bi- and polynuclear forms of general formula X_3PBY_3, X_5PBY_3, $P_2X_4 2BY_3$, $(R_2PBR_2)_n$[151] where R, X and Y may be halogen, alkyl, aryl, hydrogen etc. Of interest to this work is tribromophosphine - boron tribromide (1:1) adduct, triiodophosphine - boron tribromide (1:1) adduct, diphosphorus tetraiodide - boron tribromide (1:2) adduct, and pentabromophosphorane - boron tribromide (1:1) adduct.

According to Tarible[101] (1901) adduct formation was demonstrated by mixing and or heating phosphorus iodides (P_2I_4 or PI_3) with boron tribromide in sealed tubes. The resulting crystalline materials were shown to be the same irrespective of whether triiodophosphine diphosphorus tetraiodide was used i.e. $P_2I_42BBr_3$. It is now known with certainty that similar procedures produce two different adducts viz. diphosphorus tetraiodide - boron tribromide (1:2) adduct and triiodophosphine - boron tribromide (1:1) adduct with melting points dec. 130°C and 159-160°C respectively. Diphosphorus tetraiodide boron tribromide (1:2) adduct was soluble in boron tribromide, carbon disulphide, chloroform and insoluble in petroleum ether. The reactivity towards water was high, resulting in boric acid, phosphorus acid, hydrobromic acid and hydroiodic acid.

$$P_2I_42BBr_3 + 11\ H_2O = 2\ H_3BO_3 + 2H_3PO_3 + 4HI + 6HBr$$

Cowley and Cohen[97] (1965) undertook extensive studies of adduct formation of triiodophosphine and diphosphorus tetraiodide with boron tribromide and proposed a modification of Tarible's synthesis using carbon disulphide as solvent. The crystalline adduct diphosphorus tetraiodide - boron tribromide (1:2) adduct and triiodophosphine - boron tribromide were characterized by I.R. and X-ray techniques.

In the present investigation Cowley's method was used for the preparation of triiodophosphine - boron tribromide, while for diphosphorus tetraiodide - boron tribromide (1:2) adduct formation was conducted without solvent (see Chapter two: synthesis).

Complex formation has also been studied in detail by Armington[152] et al. (1965). The suggested method for the tribromophosphine - boron tribromide (1:1) adduct is the reaction of tribromophosphine and boron triiodide in carbon disulphide.

The synthesis of pentabromophosphorane - boron tribromide was performed by Tarible by mixing pentabromophosphorane and boron tribromide in carbon disulphide with cooling. The resulting substance was characterized by elemental analysis. It sublimes from 105°C prior to the melting point 140°C in a sealed tube. The adduct is soluble in hot carbon disulphide and is hygroscopic. It reacts with water according to the following equation,

$$PBr_5BBr_3 + 7H_2O = H_3PO_4 + H_3BO_3 + 8HBr$$

Recently (1966) the thermochemistry of some phosphorus halide-boron halide complexes has been studied by Finch[149,150] et al. The standard heats of formation have been determined and the strengths of the donor-acceptor bonds estimated. The investigation comprises of system X_3PBY_3 where X, Y = Br and I (i.e. four adducts). The bond strengths of these adducts are reported as $I_3P.BI_3$,22., $I_3P.BBr_3$,65., $Br_3P.BI_3$34., and $Br_3P.BBr_3$, 7 Kcal mole^{-1}. Similar thermochemical results for pentavalent phosphorus compounds have been reviewed by Webster[72]. The reported data for adducts are between pentachlorophosphorane (and mixed halides) with pyridine and pentafluorophosphorane with ethers and organic sulphides. There are no thermochemical measurements for 1:2 complexes such as $P_2I_4 2BBr_3$ and data for molecular adducts involving phosphorus e.g. $Br_5P.BBr_3$ are scarce.

SECTION-II. EXPERIMENTAL TECHNIQUES

CHAPTER TWO: SYNTHESIS
PURIFICATION
HANDLING
ANALYSIS

SYNTHESIS

(1) Phosphorus-Phosphorus Bonded Compounds

Pentaphenylcyclopentaphosphine - This was prepared according to the procedure of Fraxier[77] et al. Tri-n-butylphosphine (99.1g., 0.49 mol.) was added dropwise to phenyldichlorophosphine (87.7g., 0.49 mol.) with stirring in an inert atmosphere of nitrogen. The reaction vessel was cooled externally by solid carbon dioxide as the reaction was exothermic. After complete addition of tri-n-butylphosphine a rubber-like material appeared within ca. 20 min. (cf. crystalline material within a few seconds according to Fraxier[77] et al.) This material was sublimed at 120°/1 mm. Hg for ca. 3 hr. The sublimate was found to contain mainly tributyldichlorophosphorane, identified by Reinecke's salt derivative, m.p. 121° dec. (lit.[77] m.p. 121-123° dec.). The residue (pentaphenylcyclopentaphosphine) was washed with absolute ethanol and dried under vacuum for ca. 48 hr. An X-ray diffraction pattern was compared with that of an authentic sample of Daly[78] (see p. 25) and was found to be pentaphenylcyclopentaphosphine. m.p. 154° (closed capillary) lit.[61,77,78] m.p. 149-156° Yield 25.0g., 47.2% based on phenyldichlorophosphine, lit.[77] yield, 30%. (Found: C, 66.68; H, 4.87; P, 28.54. C_6H_5P requires C, 66.68; H, 4.67; P, 28.66%).

Attempted preparation of hexaphenylcyclohexaphosphine (Form B) - The procedure of Henderson[62] et al was used but with no success probably due to interconversion to the more stable Form A. (see p.28). A successful preparation was recently reported by Maier[85] using a modification of the procedure of Henderson. An authentic sample was generously supplied by Maier and was used for the thermal analysis in the present work (see p.152). Henderson's synthesis was based on the elimination of hydrogen chloride during the reaction of phenylphosphine with phenyldichlorophosphine. Phenylphosphine (3.1g., 0.028 mol.) was added, in one aliquot, to phenyldichlorophosphine (5.0g., 0.028 mol.) in dry benzene (15 ml.) under dry nitrogen. The solution was warmed at ca. 40° until gas evolution ceased. The resulting white precipitate was filtered off under dry nitrogen, followed by vacuum drying at ca. 40°/0.05 mm. Hg. On recrystallization from acetonitrile, the solid (phosphobenzene) appeared as transparent long rod-shaped crystals. m.p. 130° (lit.[62,85] for hexaphenylcyclohexaphosphine (Form B), 195-199°, 190° (open capillary); lit.[85] also described crystals of m.p. 130-155° as a clathrate in which one molecule of benzene for six phenylphosphine groups was present.). (Yield, 5.2g., 86.6% based on $C_6H_5PCl_2$).

<u>Polymeric Phenylphosphine</u> - This preparation was based on the disproportionation of phenyldifluorophosphine.[153] Phenyldifluorophosphine was prepared by a modification of the procedure of Schmutzler.[154] Phenyldichlorophosphine (143.2g, 0.80 mol.), freshly distilled at 80°/2 mm. Hg., was added with stirring to a slurry of Analar sodium fluoride, (100.9g., 1.20 mol.), dried at 400° for ca. 96 hr., in sulpholane (300 ml.) under an inert atmosphere of nitrogen. The reaction vessel contents were maintained at ca. 100° using an oil bath. The resulting material was fractionally distilled at 100°/11-12 mm. Hg. The fraction was collected under solid carbon dioxide. The colourless liquid changed to a white crystalline material on standing at room temperature for ca. 9 hr. (Cf. lit.[155] report that the material was unstable at ordinary temperature, but solidified after 1 month standing at 0°). Which was removed under nitrogen and washed with dichloromethane. The material, probably polymeric, phenylphosphine was stable in air. An X-ray diffraction pattern was compared with that of an authentic sample of Maier[85] (see p.238) which was found to be similar. The m.p. was 264-280° for Form C or D (cf. lit.[61]

m.p. 252-305°, also Form C m.p.[62] 270-283° and Form D m.p.[62,85] 260-285°), (Yield, 13.42g., 43.14% based on phenyldifluorophosphine).

Diphosphorus tetraiodide - This was prepared according to Germann and Traxler. The preparation was carried out under an inert atmosphere of nitrogen in a dry-box. Dried white phosphorus, under acetone, (2.0g., 0.016 mol. based on P_4) was scraped clean of its oxide coating and was dissolved in purified and freshly-distilled carbon disulphide (200 ml.). Analar iodine (16.38g., 0.064 mol. based on I_2) was added slowly with stirring and the reaction vessel was cooled externally by solid carbon dioxide, as the reaction was exothermic. On complete addition of iodine the solution appeared orange-yellow, and the reaction vessel was left for ½ hr. Partial crystallization of diphosphorus tetraiodide occurred. Further separation of crystals was achieved by removing some solvent under vacuum and finally filtering through a sintered funnel under vacuum. The crystals were washed with petroleum ether (b.p. 60-80°) and dried in a stream of dry nitrogen. Fine long orange-red needles of diphosphorus tetraiodide were collected, m.p. (closed capillary 124.5°, lit.[91] 124.5°, and preserved according to the technique given on p.64 (Yield, 14.90g., 81.04% based on P_4, lit.[156] 68-75%)(conventional titrimetric analysis for iodine showed 98.8% purity for P_2I_4.

(2) Phosphorus (III) Compounds

Phenylphosphine - This was prepared according to Fluck and Binder[143] and was based upon the reduction of phenyldichlorophosphine by lithium aluminium hydride. The reaction was carried out under an atmosphere of dry nitrogen. Freshly distilled phenyldichlorophosphine b.p. 80°/2 mm. Hg., lit.[145] 90-100°/15 mm. Hg. (149.0g., 0.83 mol.) in dry ether (250 ml.) was added dropwise to lithium aluminium hydride in dry ether (300 ml) in a three-necked flask equipped with stirrer. The flask was externally cooled with solid carbon dioxide. The complete transfer of phenyldichlorophosphine took 5 hrs. and then distilled water (100 ml) was added. The reaction mixture was refluxed for 4 hrs. till a white precipitate of aluminium hydroxide was visible. The liquid was filtered from the gelatinous residue. The filtrate was kept over calcium chloride for a period of 48 hrs. to remove any moisture. The supernatant liquid was decanted and distilled at atmospheric pressure to separate the ether and finally purified by redistillation at atmospheric pressure at 160° (lit.[155,157] b.p. 160°)(Yield, 70.0g., 76.4% based on phenyldichlorophosphine, lit.[155] 53.2%).

Phenyldibromophosphine - This was prepared according to the procedure of Moeller[158] et al. which is based on the exchange reaction of hydrobromic acid with phenyldichlorophosphine in phosphorus tribromide. The reaction was carried out under an atmosphere of dry nitrogen. Anhydrous hydrogen bromide from a cylinder was bubbled for 20 hrs. through a mixture of phenyldichlorophosphine (250g., 140 mol.) and phosphorus tribromide (176 ml.) in a three-necked flask fitted with a mercury seal stirrer. The mixture was maintained at refluxing temperature, ca. 173°, for 20 hrs. After refluxing, the mixture was allowed to cool to room temperature. The resulting yellow-orange liquid was initially distilled to remove the solvent tribromophosphine at 54°/11-12 mm. Hg., using oil-bath heating. This was followed by fractional distillation for phenyldibromophosphine using a 25 cm. Vigreux column insulated with cotton and asbestos packing. The fraction boiling at 84-86°/1 mm. Hg. was collected (yellow liquid). (Cf. lit.[158] b.p. 259-261°, fractionally distilled at atmospheric pressure, lit.[159] b.p. 255-257°). Yield, 230g., 61.3% (lit.[158] 80%) based on phenyldichlorophosphine, conventional titrimetric analysis for bromide indicated 99.8% purity.

Tricyanophosphine - This preparation was based on the exchange reaction of trichlorophosphine with silver cyanide (Staats and Morgan[115]). Initially, silver cyanide was prepared by mixing the solution of silver nitrate (127.4g., 0.75 mol.) in distilled water (1L.) with potassium cyanide (48.8g., 0.75 mol.) in distilled water (1L.) at ambient temperature. The resultant whitish precipitate of silver cyanide was filtered, washed with acetone, and dried in the dark under vacuum at 80°/2 mm. Hg. m.p. (silver cyanide) 320° dec., lit[157] 320° dec. (Yield, 89.6% based on silver nitrate). The same silver cyanide (50.0g., 0.37 mol.) in benzene (100 ml.) was mixed, under nitrogen, with excess trichlorophosphine (26.0g., 0.19 mol.) in benzene (50 ml.). The mixture was refluxed for ca. 24 hrs. at 80°. After refluxing, excess benzene along with excess trichlorophosphine was removed by distillation. The last traces of liquid from the white residue were removed under vacuum which was followed by sublimation, (see an apparatus on p.52) at 110°/0.05 mm. Hg. The m.p. of thrice-sublimed material (tricyanophosphine) was 190°, lit.[115] ca. 200°. lit[112] 190°. (Yield, 12.0g., 88.8% based on silver cyanide, lit.[115] ca. 81%). (Found: C, 32.77., N, 38.21., P, 28.15. C_3N_3P requires C, 33.05, N, 38.54, P, 28.41%). As a further analytical check, a sample of the material was hydrolysed to phosphorous acid[99] and hydrocyanic acid and the end-points due to these acids detected by a potentiometric titration pK[160] ($H-H_2Po_3$) = 1.8, pK[160] ($H-HPo_3^-$) = 6.15 and pK[160,161] (H-CN) = 9.14. Three end-points were detected (see graph on p.222) and calculation, on the basis of the corresponding titres, indicated a purity of 99.02% for $P(CN)_3$.

Tri(isocyanato)phosphine - This was prepared by a modification of the procedure of Forbes and Anderson[67,114] based on the replacement reaction between trichlorophosphine and silver isocyanate. Initially silver isocyanate was pre-

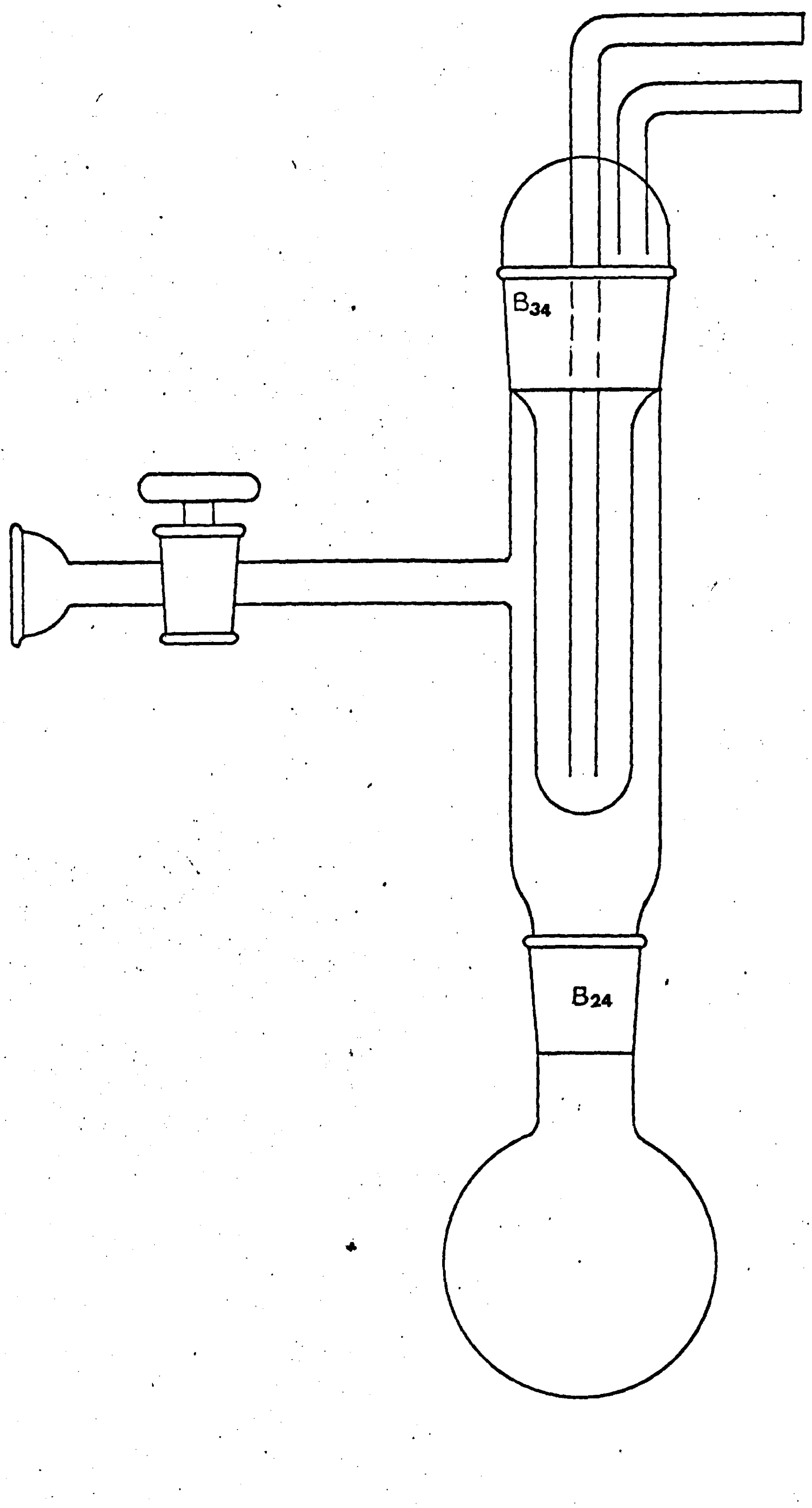


Fig. Sublimation Apparatus (x 0.50 natural size) pared by the procedure of Neville and McGee[162]. Equimolar solutions of silver nitrate (100.0g., 0.58 mol.) in distilled water (1L.) and potassium cyanate (47.7g., 0.58 mol.) in water (1L.) were mixed with stirring at ca. 0°. The resulting white precipitate of silver isocyanate (light-sensitive) was filtered off, washed with distilled water, then acetone, and finally dried under vacuum at 50°/1 mm. Hg. for 48 hrs. (Yield, 94.9% based on silver nitrate.) This silver isocyanate (83.5g., 0.56 mol.) in dry benzene (200 ml.) was added to trichlorophosphine (31.5g., 0.22 mol.) in one aliquot under a dry nitrogen atmosphere. The mixture was refluxed at 80° for 48 hrs. After refluxing, the solvent benzene, along with excess trichlorophosphine, were removed by distillation. The resulting yellowish-brown material was fractionally distilled through a 6 cm. Vigreux column at 40°/0.5 mm. Hg. (lit.[110] b.p. 60.5-63.0/10 mm. Hg.) with oil-bath heating at 60°. The first distillate was a colourless liquid b.p. 169° (lit. 169.3°[112], 160°[118]); Yield, 76%, based on silver isocyanate. The colourless liquid, after standing under nitrogen at room temperature for ca. 120 hrs., started solidifying into a whitish-yellow solid, but only two thirds of the liquid solidified over a period of 2 months. (Cf. ref.[118] notes rapid polymerization at room temperature and ref.[99] notes upon standing polymerizes to yellow-white solid.) The solid material (probably polymeric) was distilled into a colourless liquid at 40°/0.5 mm. Hg. indicating reversible depolymerisation. The freshly-distilled colourless liquid, (prior to any polymerisation), was, as a further analytical check, hydrolysed to phosphorous acid and isocyanic acid and the end-points due to these acids detected by potentiometric titration pK[160] $(\text{H-H}_2\text{Po}_3)$ = 1.8, pK[160] (H-HPo_3^-) = 6.15 and pK[117] (H-NCO) = 3.70. Three end-points were detected (as described on p.224) and on the basis of the corresponding titres for the first and third end-points indicated a purity of 98.33% for $P(NCO)_3$. The molecular weight was determined by precision cryoscopy (described on p.228) (Found: 161 $C_3N_3O_3P$ requires 157) and same sample (Found: C, 22.92., O, 30.70 (by diff.), N, 26.84., P, 19.54 $C_3N_3O_3P$. requires C, 22.92., O, 30.59., N, 26.75., P, 19.74%).

(3) Phosphorus (V) Compounds

Phenyltetrachlorophosphorane - This preparation was based on the addition reaction of chlorine to phenyldichlorophosphine in carbon tetrachloride. According to a modification of the procedure of Michaelis[146], chlorine (ca. 29g., 0.40 mol.) gas was bubbled into phenyldichlorophosphine (70.0g., 0.39 mol.) dissolved in dry carbon tetrachloride. The reaction mixture was maintained at ca. -70°. The mixture was allowed to come to room temperature, followed by refluxing for 3 hrs. After refluxing, carbon tetrachloride was removed by distillation under reduced pressure. The residue (crude, phenyltetrachlorophosphorane) turned into a viscous, creamy liquid at ambient temperature. Attempted sublimation of some of this crude material resulted in partial decomposition, presumably into phenyldichlorophosphine and chlorine. Therefore crystallization from carbon tetrachloride was carried out and resulted in long transparent rods (measuring ca. 1 by 0.2 cm.), m.p. 75° (lit. 73°[146], 75-76°[144]) Yield, 48.8g., (50% based on phenyldichlorophosphine) (conventional titrimetric analysis for chlorine showed 99.2% purity.)

Phenyltetrabromophosphorane - This preparation was based on the addition reaction of bromine with phenyldibromophosphine in carbon tetrachloride. According to a modification[159] of the procedure of Michaelis and Kohler, bromine (ca. 50g., 0.31 mol.) was added slowly and with stirring to phenyldibromophosphine (67.0g., 0.25 mol.) dissolved in dry carbon tetrachloride (250 ml.) with moderate external cooling. After complete transference of bromine, the reaction mixture was allowed to warm to room temperature, stirring continuously. After ca. 60 min. orange-yellow solid had deposited. The solid material (phenyltetrabromophosphorane) was removed under nitrogen using a sintered filter-funnel, washed with dry carbon tetrachloride, and finally vacuum-dried for ca. 8 hr. The dried powdery material was sublimed (see an apparatus on p.52) for further purification at 83°/2 mm. Hg. The purified material was in the form of long, yellow-reddish needles. m.p. (closed capillary) 207°, lit.[147] 207° (conventional titrimetric analysis of bromine after hydrolysis indicated a purity of 98.7% for $C_6H_5PBr_4$).

(4) Molecular Adducts

Diphosphorus tetraiodide-boron tribromide (1:2) adduct - This preparation was based on the addition reaction boron tribromide to diphosphorus tetraiodide. According to a modification of the procedure of Ross[97] and Tarible[101], freshly distilled boron tribromide (see p.61)(20.96g., 0.083 mol.) was added to diphosphorus tetraiodide (8.65g., 0.015 mol.) stored in a special distillation apparatus (see p.56) with occasional shaking until a golden yellow powdery material deposited (diphosphorus tetraiodide-boron tribromide adduct). After ca. 30 min. the excess boron tribromide was distilled off at ca. 25°/0.01 mm. Hg. for 2 hr. and trapped. By difference the weight of boron tribromide retained was found to be (16.2g.) i.e. 99% of theoretical 16.3g. The m.p. of the adduct, (closed capillary) was 345°-350°. It partially decomposed between 129-138° (lit.[97] describes decomposition with iodine vapour at 130° and lit.[151] 134°-136° dec.) The decomposition was investigated by thermal analysis technique (see p.159). (Conventional titrimetric analysis[160] for total halide followed by iodide gave I, 46.8., Br, 44.8, $P_2I_4 2BBr_3$ requires I, 47.41; Br, 44.8%.)

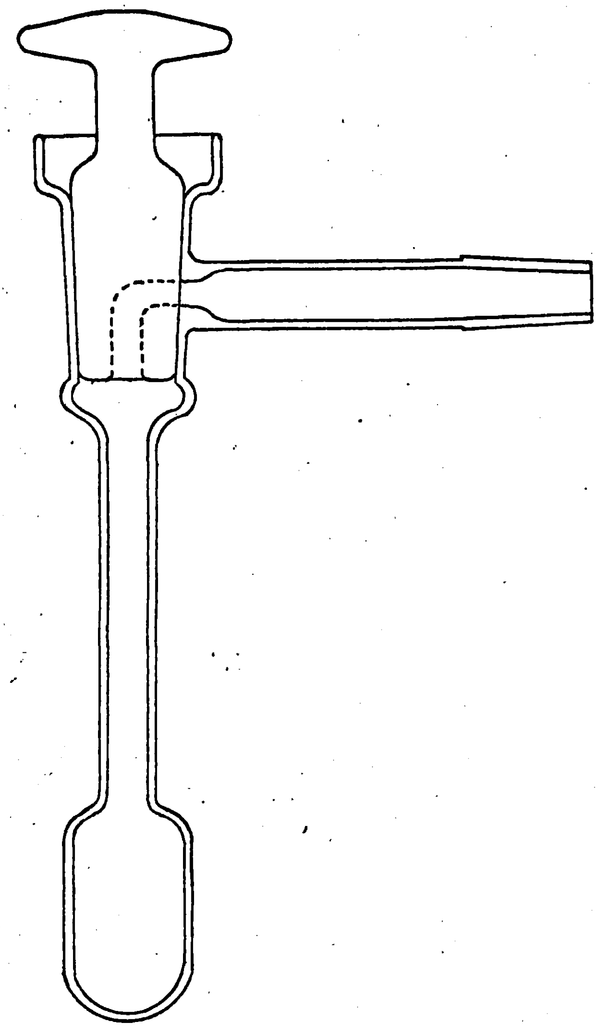


Fig. Longitudinal Section through Mixing Vessel for Adduct Synthesis(x.0.75 natural size)

Tribromophosphine-boron triiodide (1:1) adduct - This was prepared by the procedure of Armington et al.[152] The reaction was performed under nitrogen in a dry box. Tribromophosphine (6.95g., 0.026 mol.) in carbon disulphide (125 ml.) was added dropwise with stirring to boron triiodide (10.0g., 0.026 mol.) in freshly-distilled carbon disulphide (125 ml.), cooling the reaction mixture with solid carbon dioxide. After complete transference, carbon disulphide was removed under vacuum. The resulting brownish-orange solid (the impure adduct) was washed with carbon disulphide and dried under vacuum at ambient temperature. The m.p. of the adduct was 170°-182°, partially subliming at 65° (lit.[152] sublimes at 65°). The mass spectrum of this material is given on p.172. Yield, 88.7% based on boron triiodide. (Conventional titrimetric analysis[160] for total halide followed by iodide gave I, 56.68., Br, 35.79, PBr_3BI_3 requires, I, 57.49., Br, 36.20., %).

Triiodophosphine-boron tribromide (1:1) adduct - This was prepared by the procedure of Cowley and Cohn[97]. The reaction was performed under nitrogen in a dry box. Boron tribromide (6.6g., 0.026 mol.) in freshly distilled carbon disulphide (solvent purification on p.59)(100 ml) was added dropwise with stirring to triiodophosphine (5.38g., 0.013 mol.) in carbon disulphide (100 ml.) cooling with solid carbon dioxide. After complete transference, carbon disulphide was removed under reduced pressure at room temperature. The resulting reddish-yellow crystalline material (adduct) was finally dried in the dark for 10 hrs. under 0.1 mm. Hg. at room temperature. The m.p. of the adduct was 159-160° (lit.[151] 159-160° dec. lit.[152] dec. near 50°) (Yield, 5.2g., 60.4% based on triiodophosphine). The mass spectrum of this material is given on p.173. (Conventional titrimetric analysis[160] for total halide followed by iodide gave I,56.66., Br, 36.12., PI_3BBr_3 requires, I, 57.49., Br.36.20., %.)

Pentabromophosphorane-boron tribromide (1:1) adduct - This preparation was similar to that of Tarible[101,72], using methylene dichloride as solvent instead of carbon disulphide. The reaction was performed under dry nitrogen. Boron tribromide (13.10g., 0.052 mol.) in dichloromethane (200 ml.) was added slowly with stirring to pentabromophosphorane (20.0g., 0.046 mol.) in methylene dichloride (200 ml.), cooling with solid carbon dioxide. After complete transference the mixture was allowed to come to room temperature. The solvent was removed under vacuum. The resulting yellow powdery solid (the adduct) was dried under vacuum for ca. 15 hr. at ca. 25°/0.1 mm. Hg. The m.p. of the adduct was 150° (closed capillary) lit.[101] 140° (closed capillary), but partially sublimation occurred at 110°. Yield, 16.0 g., 50.5% based on pentabromophosphorane. (Conventional titrimetric analysis for bromide showed 99.6% purity. Also the bromine content was in agreement with a 1:1 adduct.) (Found: Br, 93.71, PBr_5BBr_3 requires, Br, 93.86%).

PURIFICATION

(1) Solvents

Carbon disulphide - The AnalaR carbon disulphide supplied by B.D.H. was further purified by a four-step procedure over a period of five to six days. Dissolved impurities e.g. sulphur, oxygen and moisture, have been proved to be the cause of a side reaction[91,92] when impure solvent was used for phosphorus chemistry. Initially carbon disulphide was vigorously shaken with a saturated aqueous solution of potassium permangnate (solubility, 6.48/100 ml. cold water) for a period of 48-60 hr., followed by separation of the aqueous layer. The carbon disulphide was then dried over anhydrous calcium chloride for a period of 24 hr. The decanted solvent was treated with mercury metal for 48 hr. The tarnished mercury layer was occasionally removed and fresh mercury added. Finally the solvent was fractionally distilled under an atmosphere of dry nitrogen at 46.5°/760 mm. Hg. Throughout this work, the carbon disulphide was distilled immediately prior to use.

Benzene - Analar grade (B.D.H.) benzene was distilled at 80°/760 mm. Hg. (lit. 80) and dried over sodium wire prior to use.

Ether - Reagent grade (May & Baker) was distilled at 34.5°/760 mm. Hg. (lit. 34.6) and dried over sodium wire.

Sulpholane - Pure grade (Koch Light Ltd.) was purified by distillation under vacuum at 95-96°/1 mm. Hg. (lit.[163] b.p. 283°/760 mm. Hg.) followed by drying over sodium wire.

Chloroform - Reagent grade (May & Baker) chloroform was purified by distillation at 60-61°/760 mm. Hg. before use and dried over anhydrous calcium chloride.

Methylene Chloride - Reagent grade (May & Baker) was distilled at 40°/

760 mm. Hg. (lit.[157] 40.1) and dried over anhydrous calcium chloride before use.

Petroleum Ether - Analar grade (B.D.H.) b.p. 60-80° was used directly.

Tetrahydrofuran - Reagent grade (B.D.H.) redistilled (to two-thirds of the initial volume) at 65°/760 mm. Hg. prior to use.

Pentamethyleneimine (Piperidine) - Reagent grade (B.D.H.) was distilled at 106°/760 mm. Hg. (Lit.[164] b.p. 106°).

(2) Synthetic Materials

Diphosphorus tetraiodide - This was supplied by Koch-Light Laboratory Ltd. of 99% purity. (Also synthesised see p. 49).

Phosphorus (white) - The oxide film of material (B.D.H. 99.9%) was removed by scraping under water. Before use, the phosphorus was dried with acetone.

Hexaphenylcyclohexaphosphine - An authentic sample (m.p. 190° (open capillary)) was donated by Dr. L. Maier (Monsato Research S.A., Switzerland).

Phenyldichlorophosphine - This material (Aldrich Chemical Co.) was purified by fractional distillation up an insulated 50 cm. Vigreux column. The fraction boiling at 80°/2 mm. Hg. (colourless liquid) was collected (lit.[145] 90-100°/15 mm. Hg.).

Phenyldibromophosphine - Prior to use for synthetic purpose, phenyldibromophosphine was distilled under reduced pressure. The fraction boiling at 84-86°/1 mm. Hg. (lit.[158] b.p. 259-261°, lit.[159] 255-257°) was collected (yellow liquid)(see p. 50 for synthesis).

n-tributylphosphine - A grade supplied by Koch-Light Laboratory was used without further purification.

Trichlorophosphine - Reagent grade (B.D.H.) was distilled at 75.8°/

760 mm. Hg. (lit.[157] 75.5°/749 mm. Hg.) prior to use.

Triiodophosphine - Pure grade (Eastman organic, K. & K.) was supplied. In addition, a sample (m.p. 61°), prepared by Dr. I. H. Wood[165] of this laboratory was used.

Phenylphosphine - An authentic sample of b.p. 160°/760 mm. Hg. was donated by Dr. P. Powell of this laboratory (see p. 49 for synthesis).

Tribromophosphine - Pure grade (99%) colourless liquid b.p. 172°/760 mm. Hg. (lit.[157] 172.9°) was supplied by (B.D.H.) and used directly.

Pentabromophosphorane - Reagent grade (B.D.H.) yellow crystals.

Phenylphosphinic acid - Impure phenylphosphinic acid, prepared by a procedure of Kosolapoff,[166] was twice recrystallized in dry benzene, m.p. 86° (lit.[166] 86°).

Boron tribromide - The reagent grade (B.D.H.) slightly pale yellow liquid was purified by a two-step procedure. Initially it was shaken with mercury to remove hydrobromic acid. This was followed by fractional distillation under dry nitrogen with the ground glass joints of the distillation unit connected by PTFE sleeves. The fraction boiling at 90°/760 mm. Hg. (lit.[157] 90.1°/740 mm. Hg.)(colourless liquid) was collected.

Boron triiodide - 99.9% purity (Koch-Light Laboratory Ltd.) batch No: 31845 (colourless, transparent crystals) m.p. 43° (lit.[157] m.p. 43°).

Bromine - AnalaR grade (B.D.H.) bromine of density (3.1 g./ml. at 20°) was used. The solubility was experimentally determined (titration) prior to a use for synthetic, conventional titrimetric analysis and solution reaction calorimetry.

Iodine - AnalaR grade (99.9%)(B.D.H.) was used.

Chlorine - High purity grade (99.9%) of Sp. vol. (5.4 cu. ft./lb.) was supplied by Cambrian Gases, Matheson and used directly.

Anhydrous hydrogen bromide - High purity grade, (99.8%) of Sp. vol. (4.8 cu. ft./lb.) supplied by Cambrian Gases, Matheson, was used directly.

Ferrocene - Ferrocene (B.D.H.) was twice recrystallized from absolute ethanol and sublimed in vacuo m.p. 175-176° (lit.[167] m.p. 175.5-176°). This sublimed material (yellow crystals) was used for effusion manometry (see p_{180}).

Lithium aluminium hydride - Reagent grade white powder was supplied by Koch-Light Laboratory Ltd., batch No: 30091.

Ammonium Reineckate - Reagent grade (B.D.H.) reddish-brown crystals.

Sodium fluoride - Analar grade (B.D.H.) powdered finely and dried in oven at 400° for ca. 96 hr. prior to use.

Tris(hydroxymethyl)aminomethane - High grade purity material (not less than 99.9% of pure, Aristrar) supplied by B.D.H., m.p. 171-172° was used directly for calorimetric run.

Eosin Solution - A fresh sample, used as adsorption indicator, was prepared by dissolving Eosin (B.D.H., 0.1 g.) in ethanol (100 ml. of 70% aqueous).

Diiododimethylfluorescein Solution - This was prepared by dissolving 1.0 g. substance in ethanol (100 ml. of 70% aqueous) and used as an adsorption indicator.

HANDLING

(1) Dry-Box Techniques

Dry-Box - A dry-box was designed and constructed out of 2.0 mm. thick metal at this laboratory. The dimensions (cm.) of the main body were 90 x 45 x 60, the front window (perspex) was 60 x 18 x 0.5 and the entry-port was 21 x 20 x 23. Access was via flanged (reinforced) latex gloves (scientific supplies). Throughout this work, moisture and light-sensitive compounds were handled in this dry-box. The handling of the effusion manometer containing phosphorus iodides (see p.108) was performed in a polyethylene glove bag, supplied by Instrument Research and Industry (U.S.A.) Model X-37x37. Drying in both cases was effected by trays of phosphoric oxide and calcium chloride (anhydrous). The dry atmosphere of nitrogen for the dry-box was maintained in a dynamic state using a fan driven by a 1/30 H.P. Paravalux motor. The humidity was monitored by a hair hygrometer (Fischer).

(2) Distillation Techniques

Many phosphorus compounds in the liquid state are easily hydrolysed or oxidised. Distillation of such compounds was performed under an atmosphere of dry nitrogen or dry nitrogen was flushed through distillation unit prior to the commencement. Grease of all grades was attacked by liquid phosphorus compounds and therefore PTFE sleeves (Fison Scientific) were used on all ground-glass joints. Throughout this work, unless otherwise mentioned, a two-stage rotary pump (2S20 Speedivac, Edward High Vac. Ltd.) giving 0.01 mm. Hg. was used for vacuum distillation.

(3) Filtration Techniques

Vacuum and ordinary filtration were performed in a dry-box. A vacuum sintered filtration equipment which could be easily handled in a dry-box has been designed (see Fig. on p.65). This could also be adapted for drying materials under nitrogen.

(4) Special Handling Techniques

Special care was taken with highly toxic compounds and those which were light and moisture sensitive, e.g. phenylphosphine, tricyanophosphine, tri(isocyanato)phosphine, phosphorus iodides, triiodophosphine-boron tribromide adduct.

(5) Storage

Where appropriate materials were preserved in sealed ampoules storage was at deep-freeze or at room temperatures. The following compounds were stored at -20°.

Diphosphorus tetraiodide
Triiodophosphine
Phenyltetrachlorophosphorane

A report of the hazardous nature of tri(isocyanato)phosphine[118] in the presence of moisture was noted.

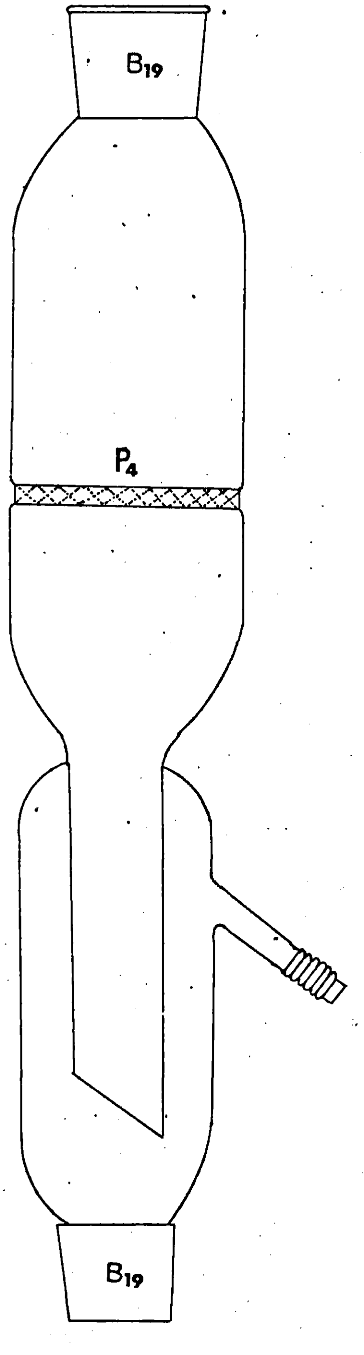


Fig. Vacuum Filtration Equipment.

ANALYSIS

(1) Microanalysis

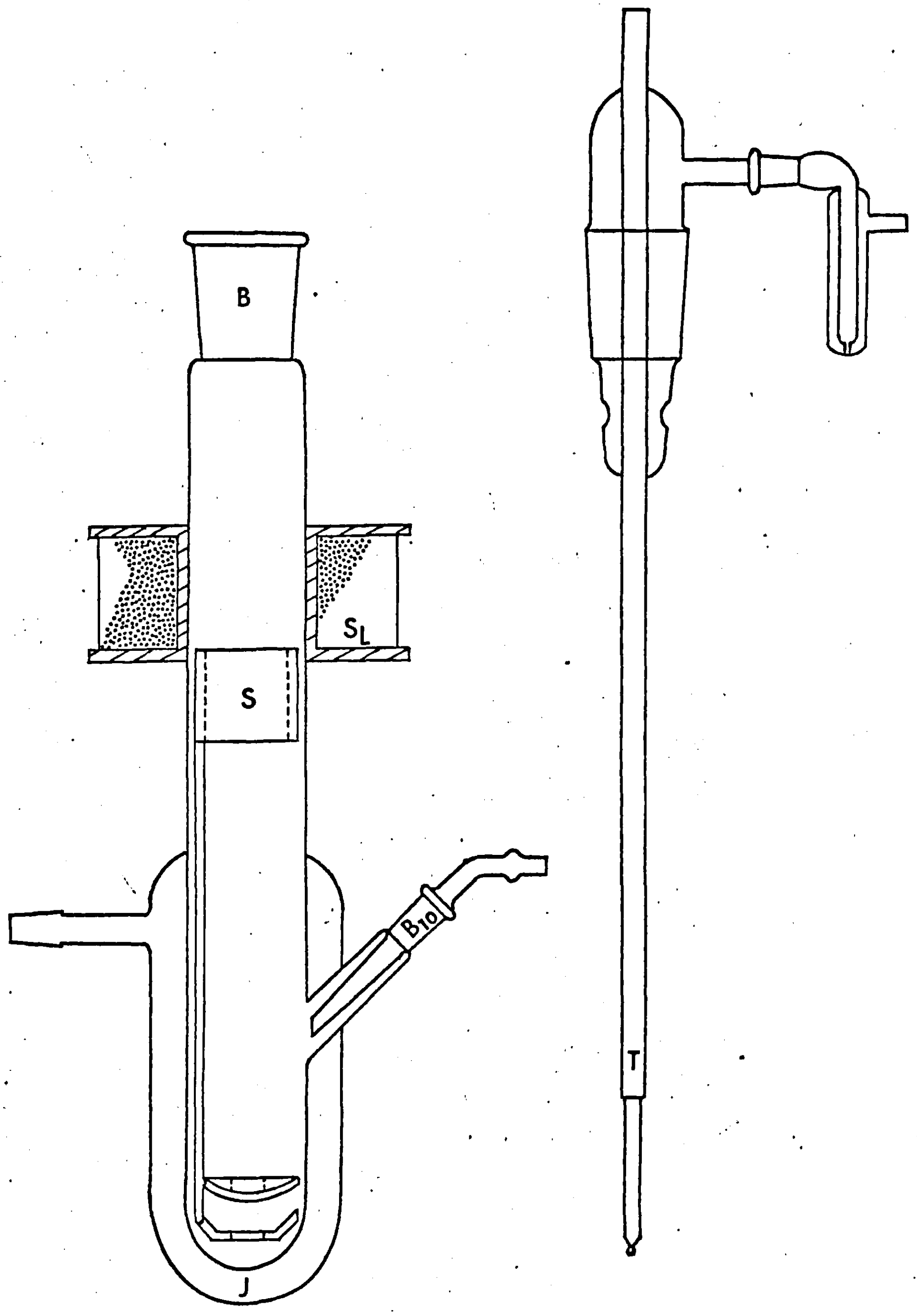
Elemental carbon, hydrogen, nitrogen, phosphorus, sulphur, analyses were carried out by Alfred Bernhardt, Microanalytisches Laboratorum, 5251 Elbach über Engelskirchen, West Germany, and also at Microanalytical Laboratory, 164 Banbury Road, Oxford.

(2) Chemical Analysis

Halides and Halogen - Halide analyses were obtained by hydrolysis of the moisture-sensitive compounds followed by conventional[160] argentiometric and iodometric titrations. The end-points were detected with eosin for total halide (e.g. bromide and iodide in $P_2I_4 2BBr_3$, PI_3BBr_3, PBr_3BI_3), with diiodo-dimethyl fluorescein for iodide, and with tetrazine for chloride (e.g. in $C_6H_5PCl_4$). In the case of the pseudohalides (e.g. $P(CN)_3$, $P(NCO)_3$), acidimetric analysis was performed on the hydrolysate. The end-points were detected potentiometrically (Pye Model 79 pH-meter). Usually three end-points were detected, two for phosphorus acid and one for the hydrogen pseudohalide, (see numerical results under synthesis p46 and titration graphs in appendix ONE p. 220).

(3) Cryoscopic Measurements

A precision cryoscope was designed in this laboratory by Finch[168] et al. for molecular weight determination of moisture-sensitive compounds. This cryoscope (see fig. on p. 67) was operated under modified conditions for phenyldichlorophosphine and tri(isocyanato)phosphine. Solid carbon dioxide in powder form was used as coolant and the air-jacket was not evacuated. All



B = Socket B24
S_L= Solenoid
S= Stirrer

J= Jacket
T = Thermistor

Fig. Longitudinal Section of Cryoscopic Cell,Solenoid and Thermistor.

transfer operations were performed under an atmosphere of dry nitrogen. The depression of the freezing point was detected by a thermistor incorporated in a Wheatstone bridge circuit. The solution was kept in a dynamic state by a specially-designed stirrer actuated externally by a solenoid (see circuit diagram on p.69). Initially the cryoscope was calibrated with naphthalene in benzene. Finely ground naphthalene was injected via a wide-bore syringe (a precision-bore glass tube and rod). The amount of substance delivered by this syringe was determined by a weight-difference method. The mode of injection in the case of phenyldichlorophosphine and tri(isocyanato)phosphine was via a weighing-pipette (Quickfit).

The molecular depression for a dilute ideal solution can be expressed as

$$\Delta Tf = Kf\ Mo$$

where

ΔTf = molecular depression

Kf = cryoscopic constant

Mo = molality of the solution

The approximate relationship for small changes in temperature and resistance for a thermistor is

$$\Delta T \propto -\Delta R$$

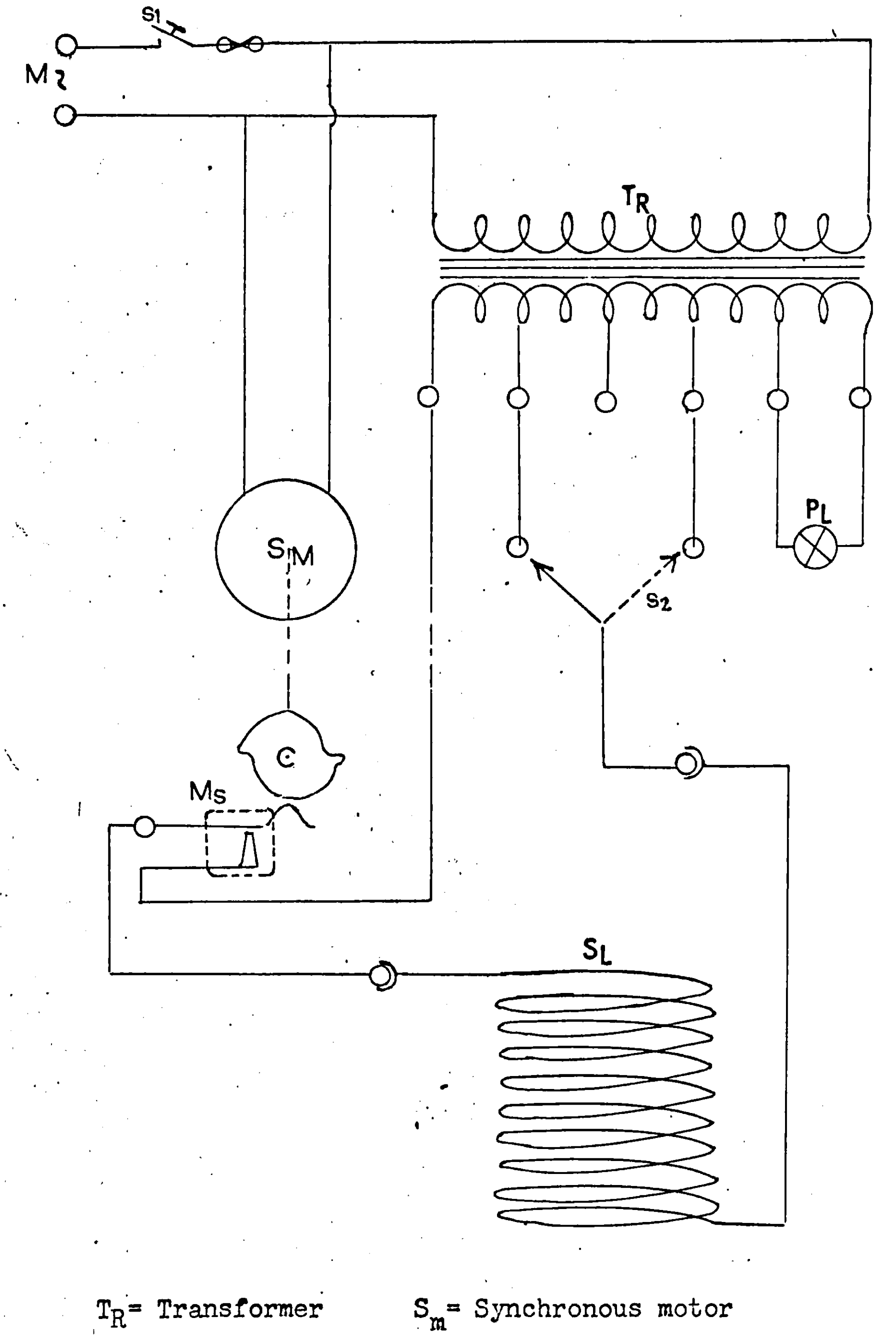
Now

$$Mo = \frac{W}{M} \times \frac{1000}{\text{weight of solvent}}$$

where

W = weight of solute

M = molecular weight of solute



C= Cam T_R= Transformer S_m= Synchronous motor

P_L= Pilot Lamp   M= Mains M_s= Micro Switch

S_1 and S_2= Switches.

Fig. Pulse Generating Circuit Diagram for Solenoid (Cryoscope).

So $$-\Delta R \quad \frac{W}{M}$$

or $$-\Delta R = K\frac{W}{M} \quad \text{for constant quantity of solvent.}$$

In practice, a graph is plotted for the depression, ΔR (in Ω) Vs W (wt. of solute in a fixed amount (usually 20g.) of benzene). The gradient for naphthalene (n) is given by,

$$Gn = \left(\frac{W}{\Delta R}\right)_n$$

substituting in $$-\Delta R = K\frac{W}{M}$$

we have $$Mn = -K\ Gn$$

So for an unknown material (x),

$$Mx = -K\ Gx = \left(\frac{Mn}{Gn}\right) Gx$$

or $$Mx = \left(\frac{Mn}{Gn}\right) Gx$$

The only unknown in this final equation is Mx, the desired quantity. The detailed numerical results obtained for $C_6H_5PCl_2$ and $P(NCO)_3$ are given in appendix two p. 225.

(4) Vibrational Spectroscopy

The structural analysis of phosphorus compounds in general[93; 169-172] and phosphorus-phosphorus bond compounds in particular[66,93,94] by infra-red and Raman spectroscopy is well-documented.

The following instruments were used in this work:

(i) Infra-red grating spectrophotometer (Unicam instrument No: 21098, s.p. 100), using KBr discs, in the range 1970 cm.$^{-1}$ to 394 cm.$^{-1}$

(ii) Infra-red grating spectrophotometer, (Perkin Elmer 337), using 0.01 m.m. cells in the range 3300 cm.$^{-1}$ to 685 cm.$^{-1}$

(iii) Raman scattering using He-Ne laser radiation (6328 A^{o}) source in a Cary 81 instrument accuracy ± 1 cm.$^{-1}$ in the range studied, 1581 cm.$^{-1}$ to 155 cm.$^{-1}$

Details of the spectrum for pentaphenylcyclopentaphosphine are presented in appendix three p.229 along with the comparison of the so-called tetraphenylcyclotetraphosphine[84] and tetraphenylcyclotetraphosphine forms A and B[172].

(5) X-ray crystallography

Structural analysis by this technique takes account of the geometrical arrangement of atoms in the lattice. This technique has been recently applied to phosphorus compounds containing the phosphorus-phosphorus bond to confirm the structures of phosphobenzene in the forms then known as $(C_6H_5P)_4$[84], and $(C_6H_5P)_4$[172], A and B. According to Daly[78,79] phosphobenzene exists as

(i) Pentaphenylcyclopentaphosphine, $(C_6H_5P)_5$, m.p. 149-150°

(ii) Hexaphenylcyclohexaphosphine, $(C_6H_5P)_6$, m.p. 190°

The crystal structures of these compounds are given on pp25,26 and the molecular stereochemistry[63] is sketched on p27. In the present work X-ray powder photographs were obtained to confirm the crystal structure of pentaphenylcyclopentaphosphine and polymeric phenylphosphine, prepared via different synthetic routes[153,173] (see pp.47,48 with that of the authentic samples of Daly and Maier respectively.

Numerical values of intensity and interplanar spacings for pentaphenylcyclopentaphosphine and so-called polymeric phenylphosphine are tabulated in appendix four on p.238.

SECTION-II. EXPERIMENTAL TECHNIQUES

CHAPTER THREE: THERMOCHEMISTRY

THERMOCHEMISTRY

(1) Solution Reaction Calorimetry - The bulk of thermochemical information is derived from reaction and combustion calorimetry and equilibrium measurements. In this work thermochemical values are experimentally determined for some phosphorous compounds by reaction solution calorimetry and where appropriate, these values are used in thermodynamic cycles. (See p. 208 for the cycle of pentaphenylcyclopentaphosphine). Two types of calorimeter were used to determine the thermochemical values, depending upon the nature of the reaction. For slow reactions (10 min. onwards) an adiabatic calorimeter was used and for fast reactions (main period complete within 10 min.) a constant-temperature-environment calorimeter was used. All measurements were made at 25°C and at atmospheric pressure.

(2) Basic Principles and Construction - The basic principles of reaction solution calorimetry are well-known.[29,34,35,174,175] A standard reference substance or electrical calibration is used for heat capacity measurements. The temperature differences and electrical energy input are determined very accurately. Thermal loss across the calorimeter boundary is commonly analysed using Newton's cooling Law. The calorimeter and its environment are treated as isothermal bodies and heat transfer between them is expressed as

$$H_t \propto T_2 - T_1$$

$$H_t = K(T_2 - T_1)$$

Where

H_t = heat transfer cal./sec.

T_1 and T_2 = low and high temperature respectively

K = constant for all conduction processes (radiation losses are neglected)

In practice the temperature gradient in the calorimeter and shield (in the case of adiabatic systems) cause a net heat exchange during the experiment. The calorimeter vessel used (for diagram see p.p.75,78) in both the adiabatic and constant-temperature-environment (abbreviated as C.T.E.) systems was similar to the original design of Finch and Gardner.[176] The temperature of the water jacket (adiabatic system) was automatically controlled (see circuit diagram p.87) so that the environment temperature was approximately equal to the internal calorimetric temperature at all times, thus minimizing thermal leakage. The accuracy and precision of this apparatus was checked using a standard reaction[177,178] (see p.117for adiabatic and C.T.E. THAM results).

A fundamental relationship for the determination of enthalpy change (ΔH) (for adiabatic and C.T.E. calorimetry) is based on the heat capacity relationship (at constant pressure). This is mathematically expressed as

$$Cp = \left(\frac{\delta H}{\delta T} \right)_p$$

Where

C = heat capacity

H = enthalpy or heat content

T = Temperature

P = Pressure

$$\text{or} \quad Cp = \frac{\Delta Hr}{\Delta Tr} = \frac{\Delta Hc}{\Delta Tc}$$

$$\text{or} \quad \Delta Hr = \Delta Hc \times \frac{M}{W} \times \frac{\Delta Tr}{\Delta Tc}$$

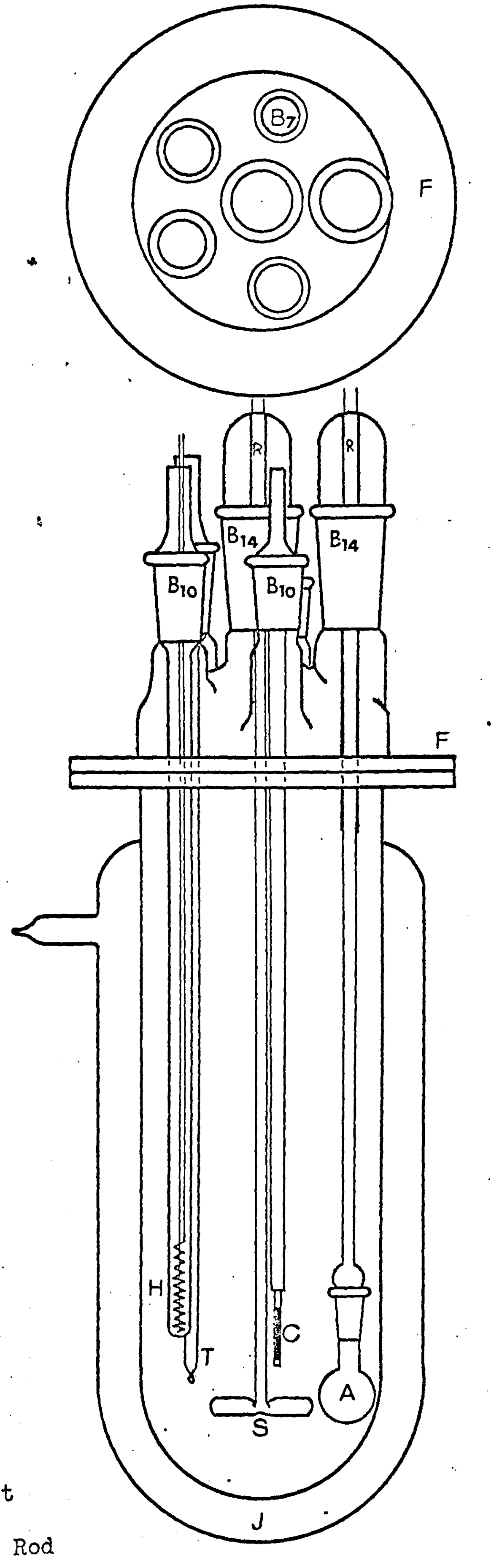
Where

r = reaction

c = calibration

M = Molecular weight

W = Weight of substance



H= Heater
T= Thermistor
S= Stirrer
A= Ampule
C= Cooling Well
J= Evacuated Jacket
F= Flange (1.5cm.)
R= Precision Glass Rod

Fig. Longitudinal Section through Calorimeter.

but ΔHc is total input of electrical energy in terms of heat content, and can be expressed as for the C.T.E. calorimeter as

$$\Delta Hc = \frac{F \times P \times t}{J}$$

Where

F = lead factor

P = power

t = time

J = 4.184 Joules cal^{-1}

For the adiabatic calorimeter F in the above expression is eliminated by precise measurement of input electrical energy in the heater windings (refer to details on p. 81).

Therefore the enthalpy change equation can be expressed as

$$\Delta Hr = \frac{(F)Pt}{J} \times \frac{M}{W} \times \frac{\Delta Tr}{\Delta Tc} \qquad (1)$$

In actual practice the term ΔT in equation (1) is expressed in terms of resistance change as the temperature sensing element is a thermistor

$$\Delta Tr = T_2 - T_1 = \frac{B}{\ln R_2/A} - \frac{B}{\ln R_1/A}$$

$$= \frac{-B \ln R_2/A + B \ln R_1/A}{\ln R_2/A \ln R_1/A}$$

Similarly $\Delta Tc = T_4 - T_3$.

Hence $\dfrac{\Delta Tr}{\Delta Tc} = \dfrac{B \ln R_1/R_2}{B \ln R_3/R_4} \times \dfrac{\ln R_3/A \ln R_4/A}{\ln R_1/A \ln R_2/A}$

Now if $R_3 \sim R_1$ and $R_2 \sim R_4$, the second term in above equation becomes unity.

So $\dfrac{\Delta Tr}{\Delta Tc} = \dfrac{\ln R_1/R_2}{\ln R_3/R_4}$

In the case of F 53 type of thermistor the following relationship was observed

$$0.1^{\circ}\mathrm{C}\ (\Delta T) \simeq 11\text{-}12\ \Omega\ (\Delta R)$$

(3) Constructional Details

The Calorimeter - The calorimeter is made up of a pyrex Dewar vessel (see p.p75,78) with internal diameter 5 cm. and depth 17.5 cm. with a rounded base. The capacity of the calorimeter cylinder is 250 ml. water. Under normal working conditions 200 ml. of fluid is used. The space between Dewar walls measures 5 mm. and is evacuated to 10^{-6} mm. Hg. for insulation. The multi-tubular lid of the calorimeter is fitted to a ground glass flanged collar. The joints are lightly greased to give a gas-tight seal. The multi-tubular lid contains six ground glass sockets usually two B_{14}, four B_{10}. The ground glass joints of B_{14} and B_{10} (or B_7) are mounted with P.T.F.E. sleeves (Fisons) to arrest the movement of the inserts during operation and to provide a gas-tight seal for operation under an inert atmosphere.

Stirrer - This is a precision glass rod the lower portion of which is converted into a double bladed propeller for downward motion of the calorimetric contents. The stirrer occupies the central position in the cylinder and is kept close to the rounded bottom of the cylinder for good circulation. The drive was effected by a 1/30 H.P. Paravalux motor (synchornous) at a constant speed of 1370 r.p.m. via a flexible cable.

Ampoule - The design of the ampoule was based on

(i) minimum glass content to be thrown in the calorimetric fluid on fracture, thereby minimizing the undesirable liberation of heat due to mechanical stirring.

(ii) rapid and complete liberation of the sample.

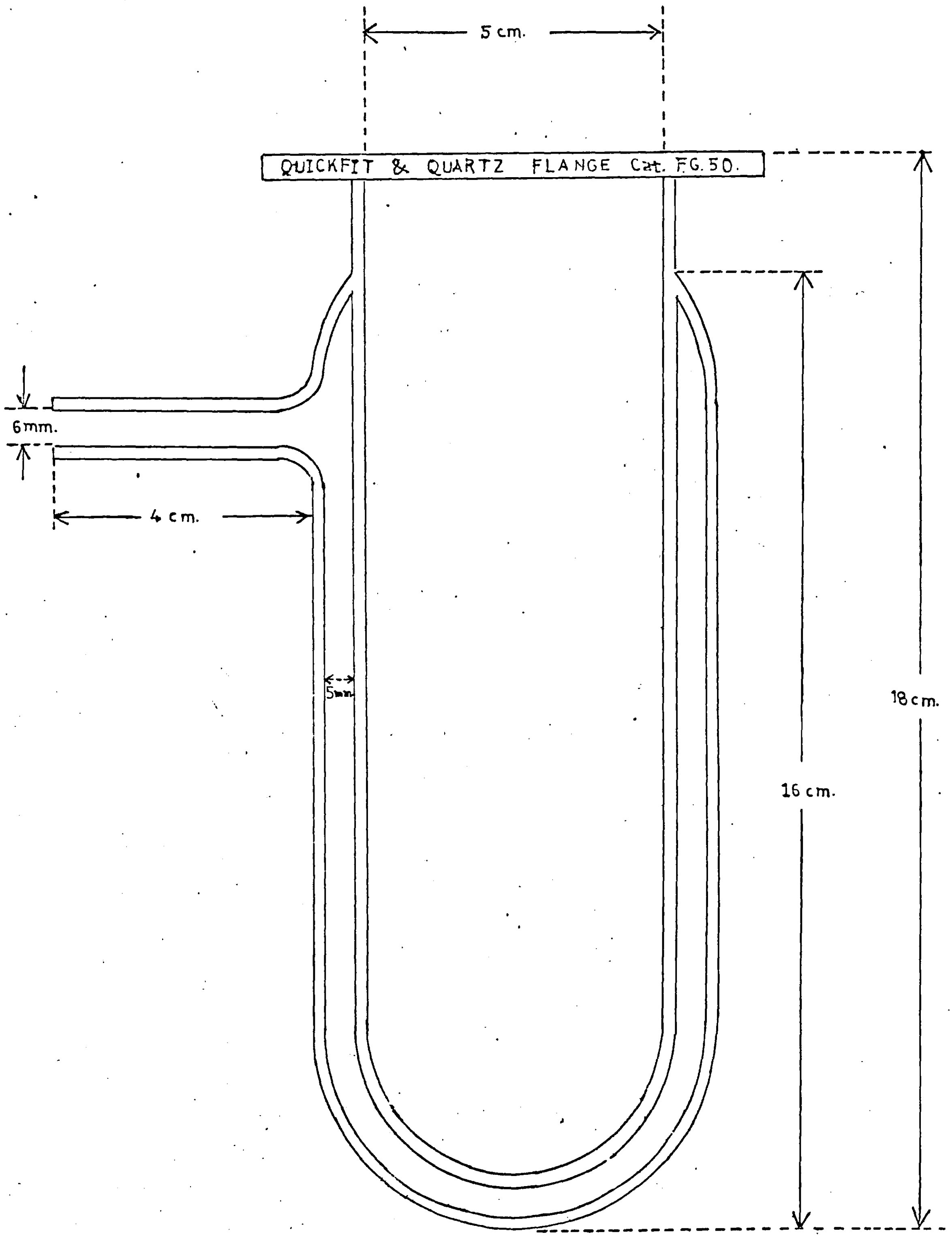


Fig. Longitudinal Section through Calorimeter Cylinder.

This was achieved by blowing onto a suitable glass tube two extremely small spherical bulbs at right angles to each other at ca. 2 cm. apart. The ampoule bulbs are fractured against the stirrer in rapid sequence for quick circulation of the calorimetric fluid.

Temperature Sensing - In the C.T.E. calorimeter a thermistor, F 53 (Standard Telephone and Cable Ltd.), was incorporated into a Wheatstone bridge powered by a 2 v. accumulator. Temperature changes were measured in terms of resistance change by a decade resistance box capable of reading to 0.1 ohm. The resistance change was recorded by a null-method, using either a 110 or 1400 ohm. Scalamp Galvanometer. In the case of the adiabatic calorimeter three F 53 thermistors were inserted. One of them served exactly the same purpose as for the C.T.E. calorimeter. The remaining two thermistors inside the calorimeter were each coupled with a corresponding thermistor outside the water jacket (an evacuated large size Dewar vessel). One pair was connected to a Wheatstone bridge and used for recording temperature differential (see p. 80). The others were sensing thermistors for the adiabatic control unit (circuit on p.87).

Calorimeter Heaters - Three heaters of resistances, 7.62, 15.631, 30.096, (for adiabatic calorimeter), 9.800 and 11.674 ohm. for C.T.E. calorimeter were made out of 42 S.W.G. constantan wire. The heater winding was specially designed to meet the requirement of complete transference of heat from wire to calorimetric fluid through the thin membrane of glass. Thin plates of mica were arranged in cross-sectional fashion with small grooves at regular intervals for equidistant winding. The ends of the constantan wire were soldered onto relatively thick copper wire (18 S.W.G.) which were in contact with the glass wall for efficient lateral flow of heat. The assembly was immersed in transformer oil, (see diagram p.75).

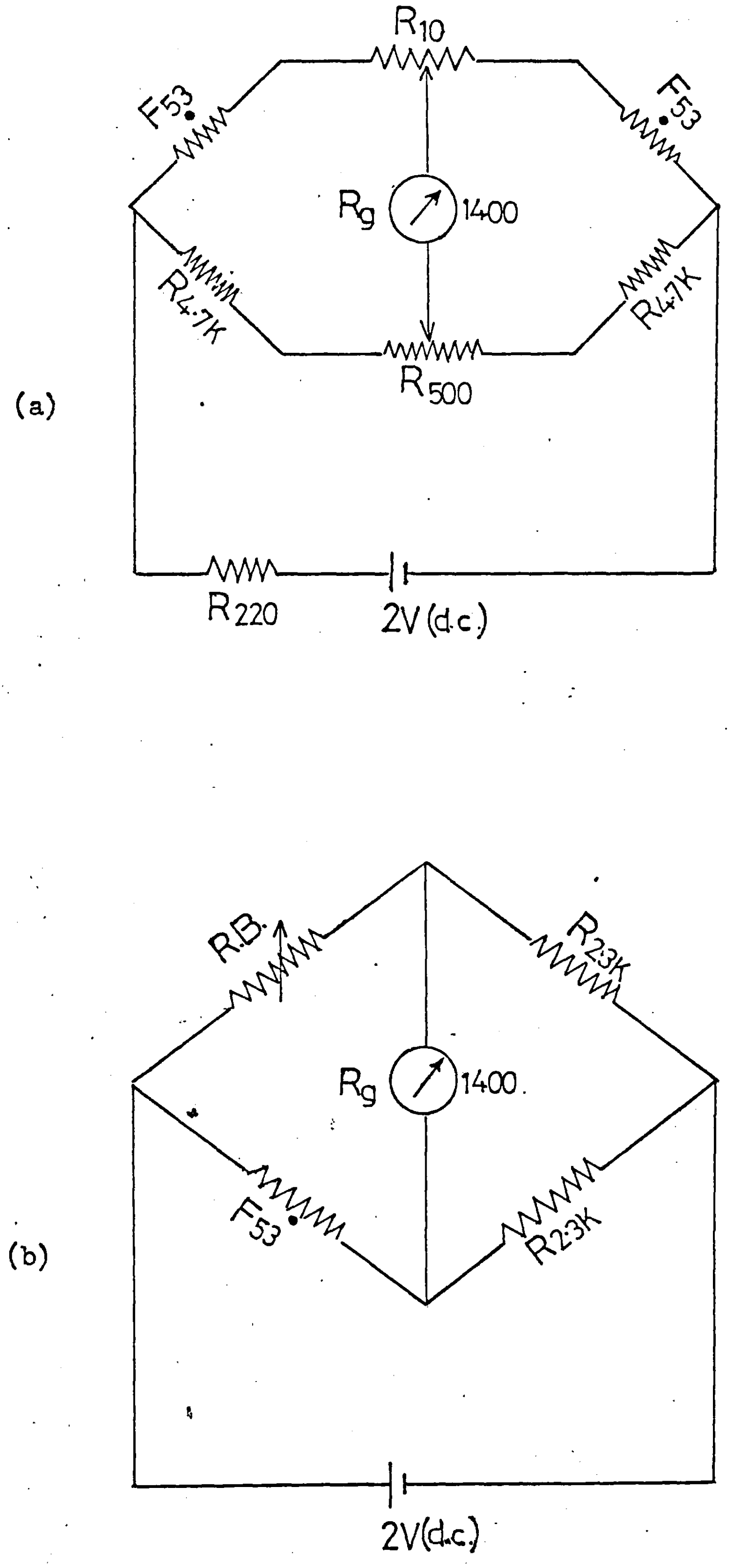


Fig. Thermistor Bridges: (a) Temperature Differential.
(b) Temperature Detection.

Details of the circuit diagram are as follows:

(i) Adiabatic calorimeter - This specially designed circuit diagram is given in fig.   on p. 82. It can be seen that the total current I flowing is given by

$$I = I_1 + I_2 = \frac{Vs}{Rs}$$

$$\text{or} \quad I_1 + \frac{V1}{10} = \frac{Vs}{Rs}$$

$$\text{or} \quad I_1 = \frac{Vs}{Rs} - \frac{V1}{10}$$

Where

Vs = potential across standard resistance Rs

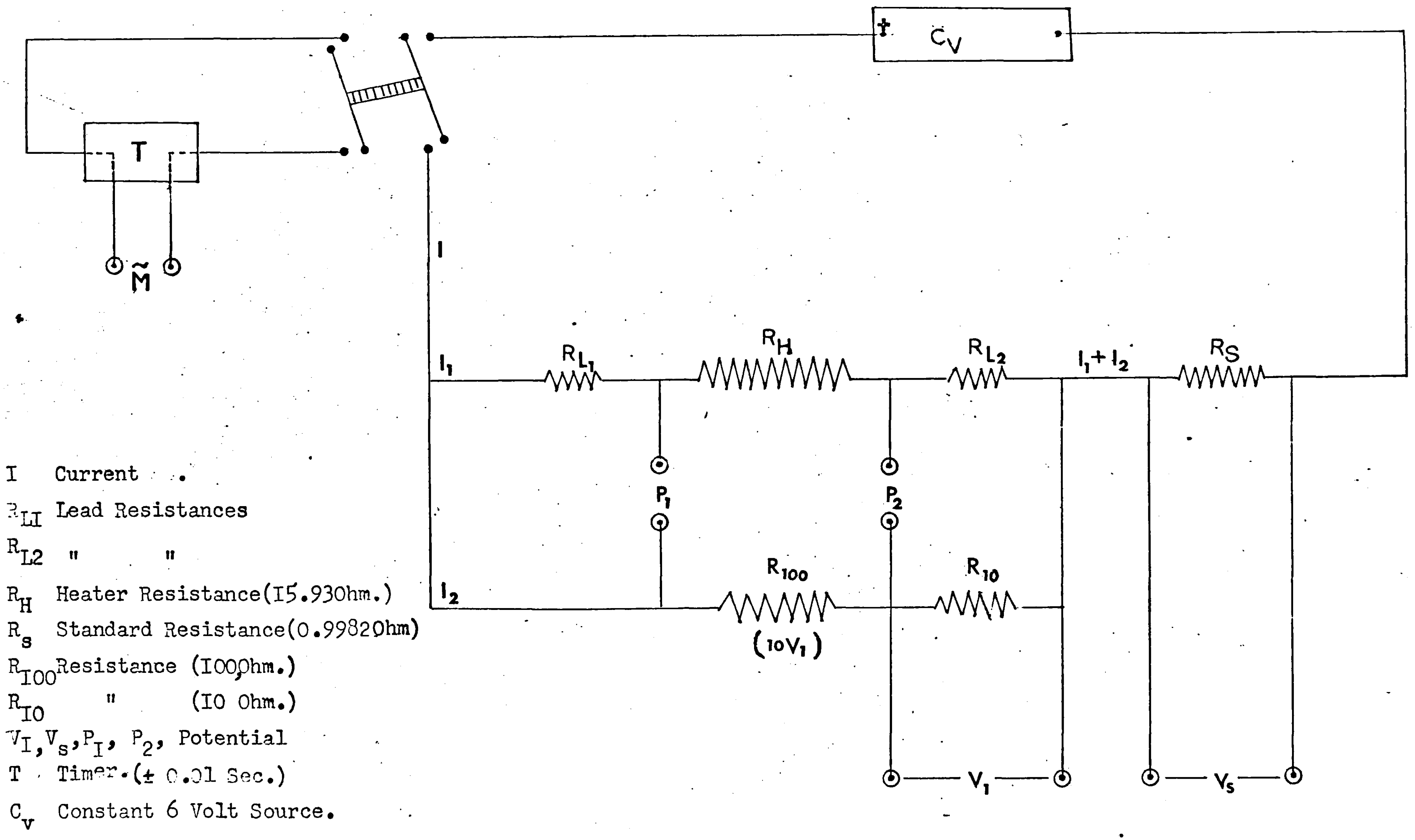
V_1 = potential across resistance R_{10}

To measure the potential drop across the heater (V_H), it is necessary to exclude the voltage across the lead resistance. Hence measurement of potentials across P_1 and P_2 is made and the relationship that expresses voltage across heater element is

$$V_H = 10V_1 + P_2 - P_1$$

In actual practice P_1, P_2, V_1, Vs are measured on potentiometer (H. Tinsley & Co. No: 187943). The potentiometer is equipped with a 2V D.C. constant voltage source (Cropico), standardized with standard cell (Weston Normal cell No: L-409188).

(ii) C.T.E. Calorimeter - In this circuit (on p.84) the potential drop across the heater (via a potential divider resistance) includes the potential across the heater leads. The power is reduced by a factor, F, to take account of this fact. From circuit it could be seen that



I Current

R_{LI} Lead Resistances

R_{L2} " "

R_H Heater Resistance(I5.930hm.)

R_s Standard Resistance(0.99820hm)

R_{I00}Resistance (I00Ohm.)

R_{IO} " (IO Ohm.)

V_I, V_s, P_I, P_2, Potential

T Timer.(± 0.01 Sec.)

C_v Constant 6 Volt Source.

Fig. Heater and Timing Circuit Diagram for Adiabatic Calorimeter.

$$R_H \text{ (calc.)} = 11\, V_1/(V_S - V_1/10)$$

$$F = R_H \text{ (actual)}/R_H \text{ (calc.)}$$

and

$$P = 11\, V_1\, (V_s - V_1/10)$$

V_1, V_s are measured by a potentiometer similar to that used for the adiabatic calorimeter (see above). R_H (actual) is measured accurately during heater construction using probe leads across the windings only.

TABLE - Some typical potential readings obtained with different heaters are as follows

(i) Adiabatic calorimeter

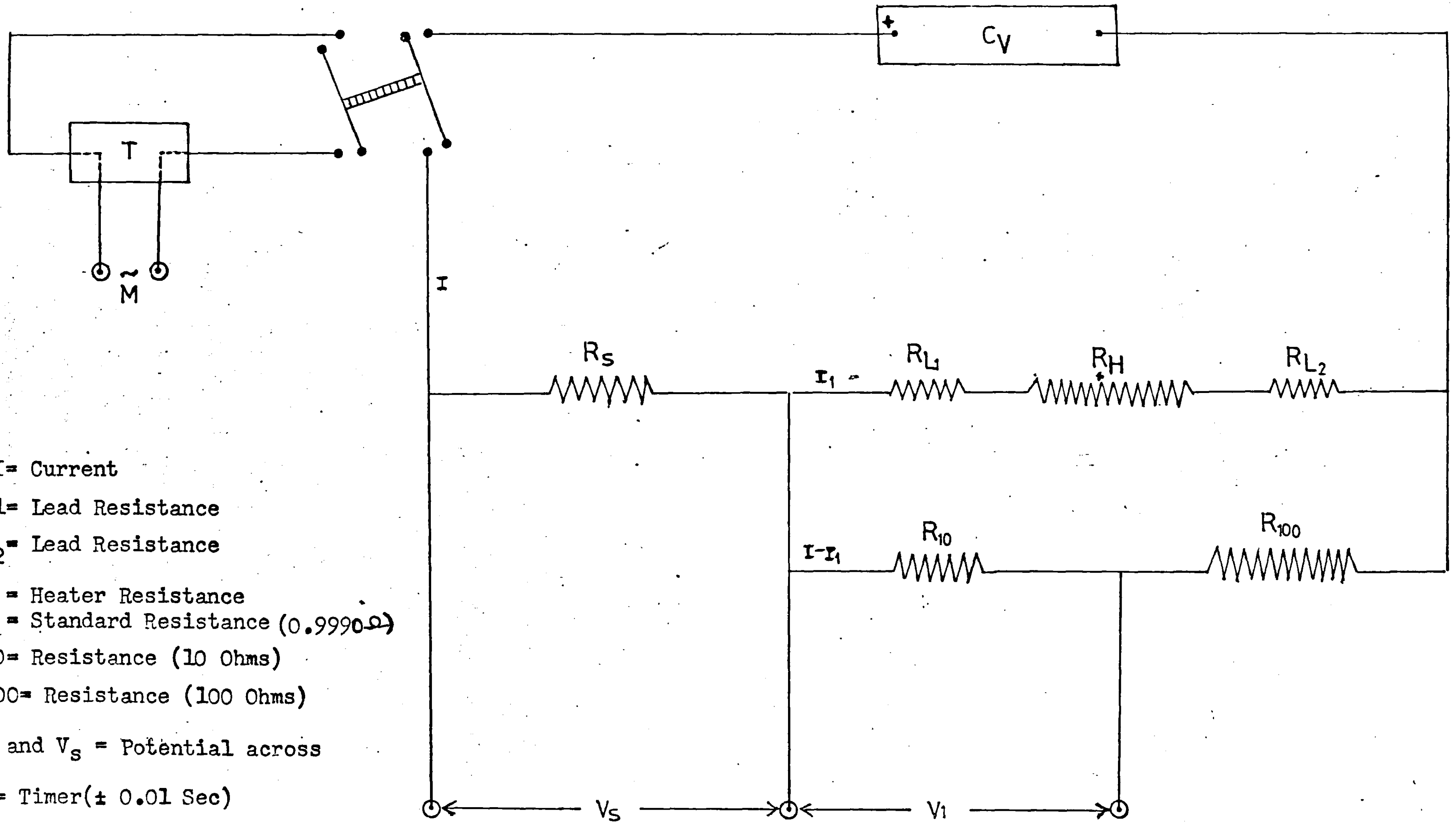
RH (ohm)	Vs (volt.)	V1 (volt.)	P1 (volt.)	P2 (volt.)
7.672	0.5935	0.3926	0.0245	0.3583
15.601	0.3357	0.4202	0.0160	0.4023
30.006	0.2014	0.4338	0.0108	0.4221

R_H = Heater resistance (25°), V_s = potential across standard resistance (0.9982), V_1 = potential across 10 ohm. resistance, P_1 = potential after lead resistance RL_1, and P_2 = potential before lead resistance RL_2

(ii) C.T.E. Calorimeter

RH (ohm.)	Vs (volt.)	V1 (volt.)
9.800	0.5740	0.4800
11.674	0.5025	0.4883

R_H Heater resistance (25°), V_s = potential across standard resistance, V_1 = potential across resistance (10 ohm.)



I= Current
R_{L1}= Lead Resistance
R_{L2}= Lead Resistance

R_H = Heater Resistance
R_s = Standard Resistance (0.9990 Ω)
R_{10}= Resistance (10 Ohms)
R100= Resistance (100 Ohms)

V_I and V_s = Potential across

T = Timer(± 0.01 Sec)

C_V= Constant Voltage Source

Fig. Heater and Timing Circuit Diagram for C.T.E. Calorimeter.

The Adiabatic Control Unit - Circuit diagram for this control unit is shown in Fig. on p. 87 and is responsible for detecting and maintaining a negligible temperature differential across the boundary wall of the calorimeter. The circuit is a modification of the design of Raymond[179] et al. In this work 25 W. monitor heater and 250 W. booster heater with the latter coupled through a variac transformer was satisfactory.

(4) Operating Procedure

(i) Adiabatic Calorimeter - The loaded calorimeter (as on p. 75) was immersed and clamped in a vertical position inside the unsilvered pyrex Dewar (an adiabatic shield) containing 4 litres of stirred water. The temperature inside the calorimeter was maintained at ca. 25°. Fluctuations in temperature were adjusted by the adiabatic control unit. Care was taken to maintain a small heat transference value across the boundary of the calorimeter to compensate for the heat of stirring. Fore-run readings were taken on a Scalamp Galvanometer at $\frac{1}{2}$ or 1 min. intervals after the calorimeter acquired the thermal equilibrium (in ca. $\frac{1}{2}$ hr.). The fracture of the ampoule containing the sample initiated the reaction. An exothermic reaction gave a decrease in resistance and endothermic reaction an increase. Reading during this period following ampoule fracture was the after-run.

Graphical extrapolation of the fore-run reading to the start of the reaction gave R_1 and back extrapolation of the linear part of the after-run reading to the same time, gave R_2. Using the same procedure over a similar temperature range for the calibration gave R_3 and R_4.

(ii) C.T.E. Calorimeter - Operating procedure was similar to above. The loaded calorimeter was immersed in water tank whose temperature (± 0.01°) was automatically controlled by a relay system.

In both C.T.E. and adiabatic system value of R_1 and R_2, R_3 and R_4 were obtained from resistance vs. time graph (see p.116) and from the equation, enthalpy of reaction was obtained.

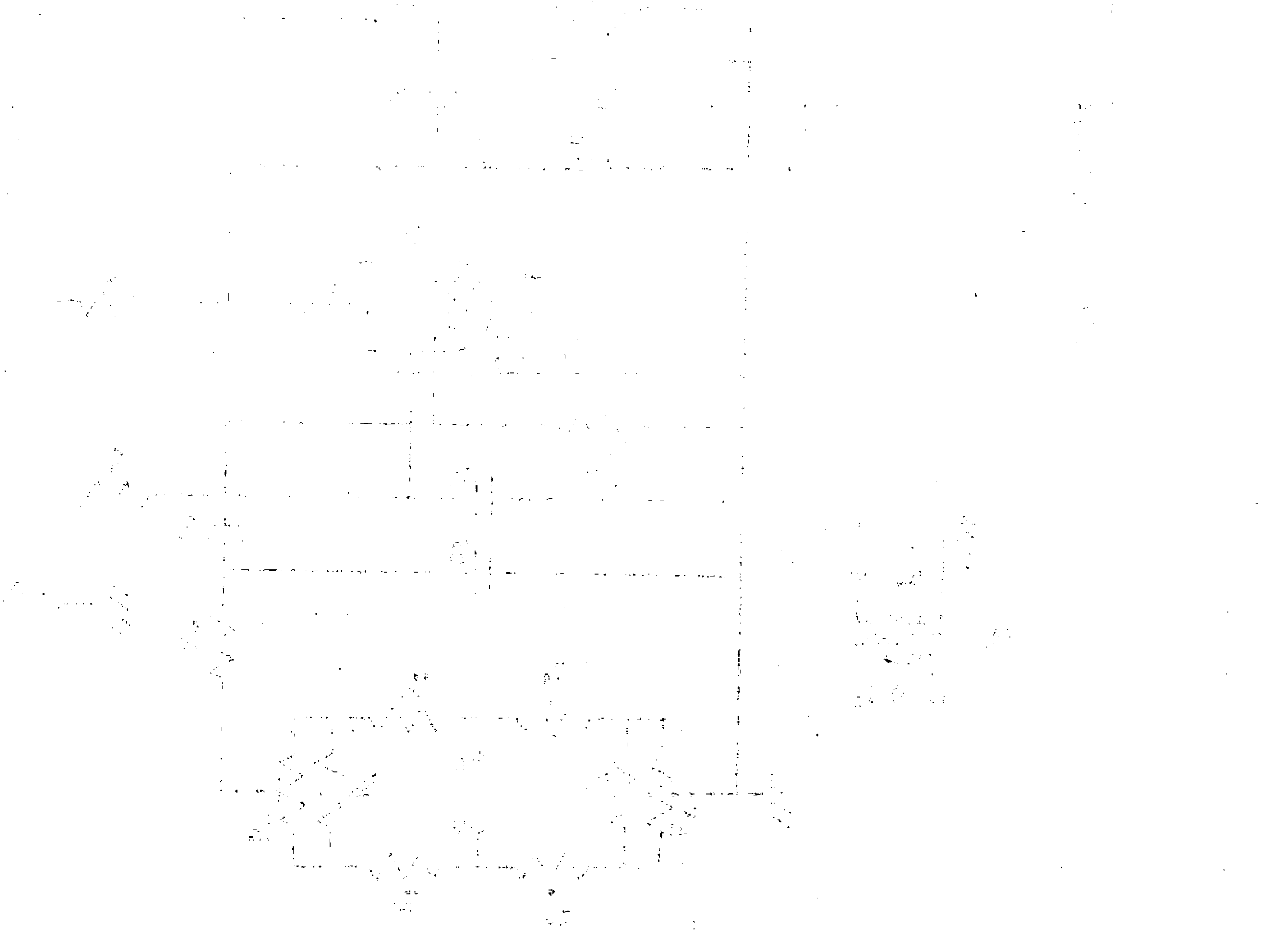
$$\frac{\text{Heat of reaction}}{\text{Heat of calibration}} = \frac{\log R_1/R_2}{\log R_3/R_4}$$

$$R_1 > R_2, \quad R_3 > R_4$$

A detailed procedure for a typical C.T.E. and adiabatic runs for the heat of neutralization is given in Chapter Six p.109.

(5) Electronic Circuit for Adiabatic Control Unit

In the following figure and table details of the Adiabatic Control Circuit are given:



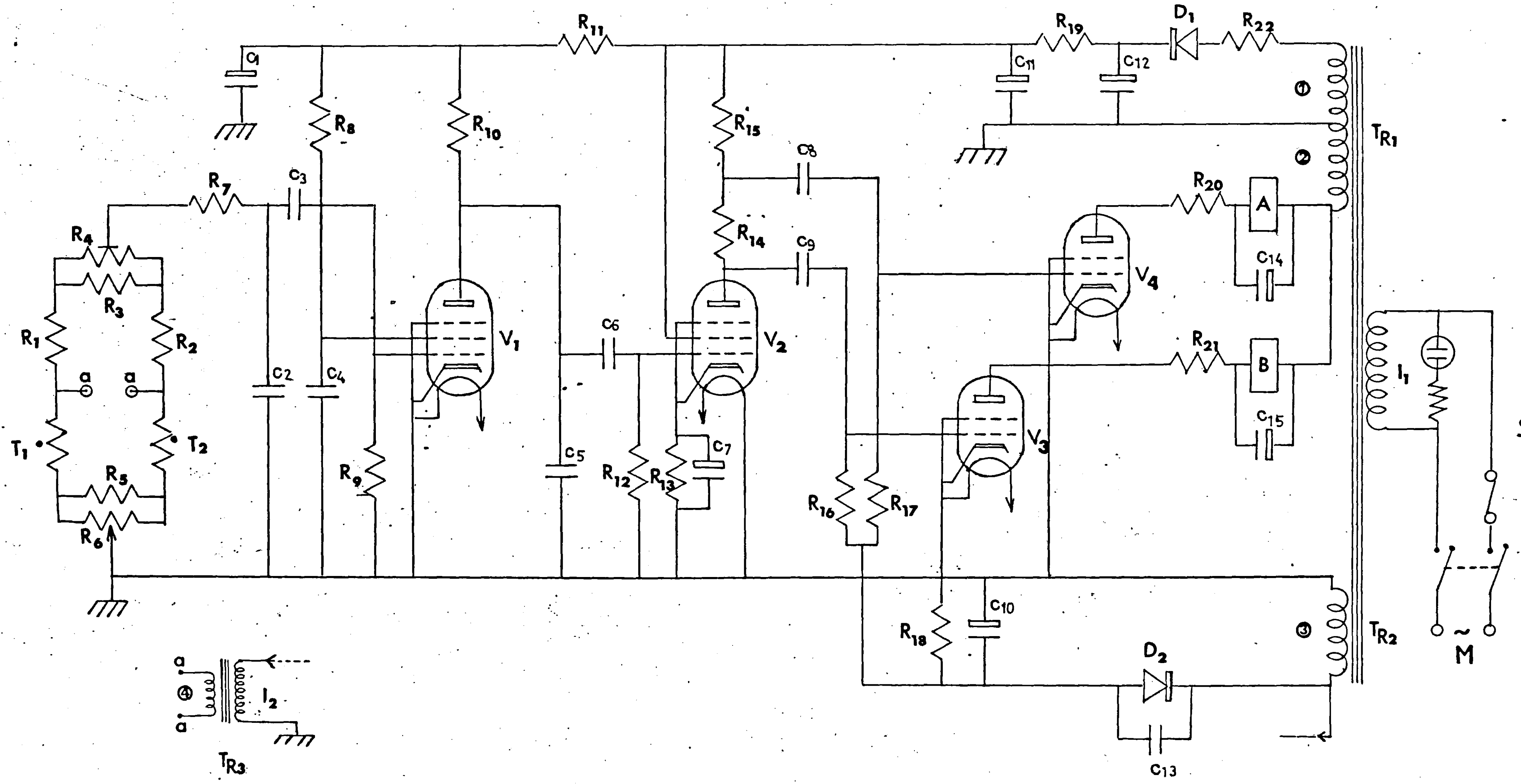


Fig. Circuit Diagram of the Adiabatic Control Unit (see pp.88,89 for details)

TABLE Electrical components of the Adiabatic control unit

RESISTANCES		CAPACITORS	
SYMBOL	VALUE (Ω)	SYMBOL	VALUE (μF)
R_1	2K	C_1	16
R_2	2K	C_2	0.01
R_3	150	C_3	0.01
R_4	500	C_4	0.5
R_5	15	C_5	0.02
R_6	100 (WW)	C_6	0.02
R_7	10K	C_7	50
R_8	1M	C_8	0.004
R_9	10M	C_9	0.004
R_{10}	220K	C_{10}	50
R_{11}	22K (1W)	C_{11}	16
R_{12}	1M	C_{12}	16
R_{13}	270	C_{13}	0.005
R_{14}	3.9K	C_{14}	8
R_{15}	4.7K	C_{15}	8
R_{16}	1M		
R_{17}	1M		
R_{18}	47K		
R_{19}	4.7K (2W)		
R_{20}	5K (5W)		
R_{21}	5K (5W)		
R_{22}	21 (5W)		

V_1	Pentode valve, EF 86 Type, for signal voltage amplifier
V_2	Pentode valve, EF 91 Type, for signal voltage amplifier
V_3	Tetrode valve, 2D21 Type, for power amplifier
V_4	Tetrode valve, 2D21 Type, for power amplifier
A	Relay post office 5000 Type to booster-heater 250W
B	Relay post office 5000 Type to monitor-heater 25W
D_1	Diode OA81 Type
D_2	Diode OA81 Type
T_1	Thermistor F23 (Standard Telephones and Cables Ltd.)
T_2	incorporated to A.C. Wheatstone bridge circuit
a,a	Connections for 3 V.A.C. bridge supply from transformer TR_2
TR_1	Step-up transformer from 250v. to 500v.
TR_2	Step-down transformer from 250v. to 6.3v.
TR_3	Step-down transformer from 6.3v. to 3v.
M	Mains, 250 V.A.C.(50 c.p.s.)
I_1	Input 250v. to step-up transformer TR_1
I_2	Input 6.3v. to step-down transformer TR_2
①	Output 250v. converted to D.C. voltage by built in E.H.T. for anodes of pentodes
②	Output 250v. to relays
③	Output 6.3v. to negative bias device
④	Output 3v. to A.C. Wheatstone bridge

SECTION-II. EXPERIMENTAL TECHNIQUES

CHAPTER FOUR: (A) THERMAL ANALYSIS
(B) MASS SPECTROMETRY

(A) THERMAL ANALYSIS

(1) Thermal Analysis - This technique makes use of the fact that the physical or chemical properties of the substances may change as a function of temperature. The theoretical and practical aspects of the subject are well-established[42,180,181]. This has resulted in the commercial construction of various types of thermal analyzers, while the growing importance of this technique has resulted in a wide range of applications in the fields of physical[45,46,182], analytical[46], organic[46,48] and inorganic[45,46,182] chemistry. The recent publication of two new journals called "Thermochemica Acta" (Jan. 1970) and "Thermal Analysis" Quarterly (fr. Hungarian Academy of Science, in press) testifies to the scope of the subject. This technique has been used for the measurements of (i) transition energy involved at a phase change and (ii) relative dissociation energy in certain phosphorus compounds (see p.p. 159,16 under thermal analysis results).

Usually the results derived from thermal analyzers are based on the methods of Thermogravimetric analysis (TGA); Thermomagnetic analysis[183] (TMA); Electrical thermal analysis (ETA); Differential thermal analysis (DTA) and Differential Scanning calorimetry (DSC). Very often TGA is combined with DTA or DSC and has proved to be a most versatile combination. Most of these analyzers are designed to handle a milligram quantity of substance with a high degree of accuracy and precision. In the present work TGA (Netzsch and Du Pont), DTA (Du Pont) and DSC (Perkin Elmer) were used.

(2) Thermogravimetric analysis (TGA) - This method is based on weight loss (or gain) as a function of temperature or time. Hence in practice a thermogram of weight loss against temperature is recorded on a linear (or

time base X-Y) recorder. The pyrolysis curve is then analysed primarily for decomposition modes, followed by detailed investigations from the derivative graph (of weight per unit time vs. temperature).

Since this method is based on weight loss under the conditions of heating, a thermobalance of high precision is an essential requirement. A detailed discussion of thermobalances has been published[184,185]. In practice these balances are classified as semi-micro, micro and macro, depending upon the quantity of sample that could be handled for analysis. The thermobalances used here are semi-micro and micro types.

(3) Differential Thermal Analysis (DTA) - This method produces a plot of the difference between the sample temperature and an inert reference temperature vs. the environmental temperature. In this type of analysis a micro quantity (mg.) of sample is placed in small metallic pan and subjected to a controlled programming of temperature simultaneously with an inert reference sample (usually alumina). Both these specimens are heated simultaneously on the same platform. The difference in temperature between the two specimens is recorded as a thermovoltage by a thermocouple and fed via an amplifier to an X-Y recorder (see diagram on P. 93). When a phase transition occurs in the sample under study, ΔT becomes negative or positive. The area between the peak and the base line corresponds to the heat content requires for the transition to occur. In the present work, thermal analyses were performed on a Du Pont 900 thermal analyzer (basic unit) along with a DTA cell (850°C) using a nitrogen flow and a quartz cover for the DTA cell.

(4) Differential Scanning Calorimetry (DSC) - This method is based on a compensation principle whereby temperature differences produced by the

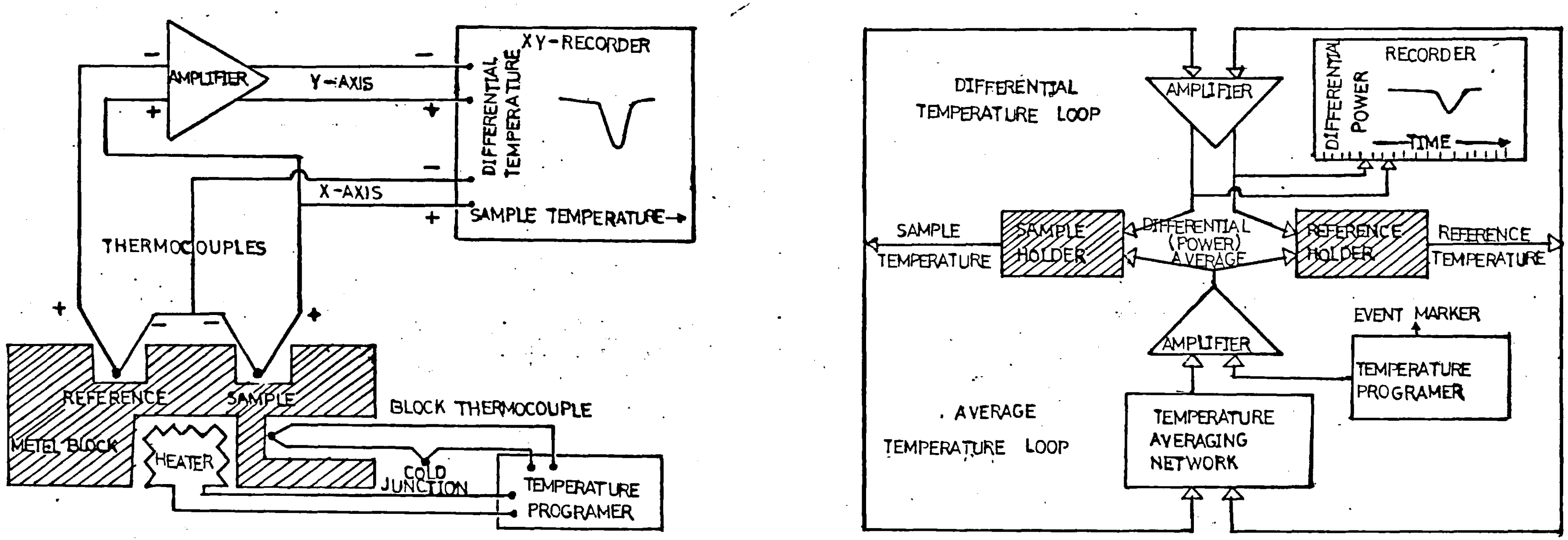


Fig. (a) Block diagram of Differential Thermal Analyzer measuring actual temperature change in a sample and records ΔT vs. T.

(b) Block diagram of Differential Scanning Calorimeter measuring power required to control a temperature change and records Calories sec^{-1} vs. Temperature.

sample undergoing a phase transition are compensated by suitably controlling the source of heat to the sample. In actual practice the equipment is so designed (see block diagram on P. 93) to measure the differential energy required to keep both sample and reference at the same temperature throughout the analysis, and records calories per second vs. temperature. The area under the peak gives a direct measure for the transition enthalpy. With suitable calibration this technique may be used to measure the heat capacities' and the energies associated in endothermic and exothermic process. Heats of transition are measured with reference to standard substances (usually indium) whose specific heat is well known. Such a procedure is also adopted here to find the transition energy of the phosphorus-phosphorus bonded compounds and their molecular adducts. In practice the indium peak area (P_{In}) is expressed as

$$P_{In} = \text{Weight of In} \times \text{Specific heat of In}$$

and also

$$P_{Sample} = \text{Weight of Sample} \times \text{Specific heat of Sample}$$

Therefore with reference to indium the heat of transition (or heat of fusion, $\Delta H_{fus.}$) of unknown sample could be expressed as

$$\Delta H_{Sample} = \frac{P_{Sample}}{P_{In}} \times \frac{\text{Weight of In}}{\text{Weight of Sample}} \times \Delta H_{fus}\ \text{In}$$

P = peak area

ΔH_{fus} In = 6.79 cal.g^{1-}

The type of thermal analyzer employed for this work was the DSC-1B (Perkin Elmer). Full details of the instrument and its operational principles and procedure are discussed in the commercial manual.[186]

(5) Standard Test Materials - Recently a possible list of standard test materials covering a wide range of temperature and heat content measurement using DTA has been published by Garn[44]. This list includes potassium nitrate, potassium sulphate, potassium chromate, potassium hydrogen sulphate, potassium persulphate, silver sulphate, silicon dioxide, barium carbonate and aluminium oxide. Indium[48] is selected as the standard reference for DSC measurements for the following reasons (i) material of high grade purity is usually available (claimed to be 99.9999% pure[48]), (ii) the specific heat is well-known, (0.057 cal. $g.^{-1}$ $^{o}C^{-1}$), (iii) the temperature reproducibility (i.e. 156.5°, see P.147 for thermogram) at the melting point is excellent, (iv) on fusion, indium produces a sharp peak with a minimum transition temperature range. In the present work all the DSC results for transition energy calculations are measured against an indium standard.

(B) MASS SPECTROMETRY

(1) Mass Spectrometry - The use of a high-energy electron beam to split up molecules into fragment particles, and subsequent collection of these particles by means of an electric and magnetic field mutually at right angles, is the basis of mass spectrometry. The theoretical and practical background to the subject is now well-known and well documented[41,187-191]. Thermodynamic data obtained from electron impact studies for phosphorus compounds[41,188,189] in general, and phosphorus-phosphorus bonded[73,74,192] compounds in particular, are discussed in this thesis; electron impact studies are also extended to include the molecular adducts of phosphorus and certain phosphorus (III) compounds. e.g. triiodophosphine, diphosphorus tetraiodide, tribromophosphine-boron triiodide (1:1) adduct, triiodophosphine-boron tribromide (1:1) adduct, boron triiodide, tribromophosphine, and boron tribromide. Detailed results are presented in chapter 8 on P.161 .

The basic quantitative equation for ion collection is

$$\frac{m}{e} = \frac{H^2r^2}{2v}$$

Thus it can be seen that the mass to charge ratio (m/e) is proportional to the square of the radius of motion (r) of the ion for constant field (H) and accelerating potential (v).

Molecular ions and atomic ions are formed whenever collision occurs with an electron having energy equal to, or greater than, the ionization energy of the molecule or atom (ionization energies range between 7 to 15 ev and bombarding potentials are commonly 70 ev). If the electron energy is below the ionization energy no ions are formed. Thus in actual operation it can be seen that the intensity of the ion current decreases steeply as the electron bombarding energy is lowered. In practice, ion current (usually positive or negative) is plotted against electron energy expressed in electron volt (ev). The shape of the curve obtained for positive ions is sigmoid, with tailing portion exponential in character, while for negative ions it is a sharp or broad peak followed by a sigmoid-like curve. The units for ion current are either expressed in microamperes or cross-section for ionization (i/e units of 10^{-16} cm^2) or arbitary units.

It is observed that increase in electron energy beyond 70 ev has little effect on the magnitude of ion-current and the curve obtained is relatively insensitive. Therefore an electron energy beam of 10 - 70 ev is commonly used for analytical purposes. In this work appearance potentials were obtained in order to derive bond dissociation energies in triiodophosphine and in diphosphorus tetraiodide. Relevant results and the thermochemical cycles[192] using these appearance and ionization potentials are given on pp.164-166 The cracking pattern in molecular adducts like I_3P - BBr_3, Br_3P - BI_3 and those concerning phosphorus (III) compounds like PI_3, BI_3, PBr_3, BBr_3 are also discussed.

<u>(2) The determination of appearance potential from Ionization Efficiency Curve (I.E.C.)</u> - Various treatments[187,190] have been advanced, some empirical and others based on energy-compensating principles to derive accurate values of ionization and appearance potentials. In the present work the semi-logarithmic plot method of Lossing[194] was used with argon as internal standard. The appearance potential measurements were performed using an AEI model MS2H mass spectrometer (in collaboration with Mr. M. Paul of the Explosives Research Development Establishment (E.R.D.E.)) with a direct inlet system for solid samples of PI_3, and P_2I_4.

Application of appearance potential (A.P.) and ionization potential (I.P.) data to thermodynamic problems[73,74,187,190,191,213] Many thermodynamic functions are obtainable from appearance and ionization potential measurements e.g. electron affinity, proton affinity and bond dissociation energies (D or B.D.E.). A relationship for bond dissociation energy in terms of ionization and appearance potentials is

$$D(R - x) = A.P.\ (R^+)_{Rx} - I.P.(R) - KE - E_{Excitation} \quad \ldots\ldots\ldots\ldots (1)$$

where

Rx = molecule (under consideration)

$K.E$ = kinetic energy of R^+, < 0.2 ev

$E_{Excitation} = 0$ as the reference states with respect to the neutral molecule and ion (parent or fragment (s)) are taken as ground states (i/e lowest vibrational level of the nuclei of the molecule).

Thus it can be seen that by definition A.P. is the minimum electron energy required to produce an ion (or fragment ion) along with a neutral fragment, and I.P. by definition is the minimum energy required to remove an electron to produce a parent-ion from the neutral molecule.

Comparing ionization process with ionization from electron impact, a small difference in energy sometime occurs due to the kinetic energy imparted to the ion by accelerating voltage. If the kinetic energy imparted to the ion is ignored, then a relationship with thermochemical data can be derived for the appearance potential (A.P.) and bond dissociation energy(D).

SECTION-II. EXPERIMENTAL TECHNIQUES

CHAPTER FIVE: EFFUSION MANOMETRY

Effusion Manometry

(1) Effusion Manometry - This technique is based on an isothermal gas transportation mechanism at low applied pressure with negligible molecule-molecule collisions as compared with molecule-wall collisions at the orifice (or porous medium). The molecules in the effusing gas under such conditions possess no turbulent flow which is the essential condition for this mode of gas motion. Therefore a relationship for the conversion of the material loss to equilibrium vapour pressure can be derived on the basis of the kinetic theory of gases. In practice this relationship is well-established[76,195-205] for the measurement of vapour pressure. Usually this technique is applied for substances having low vapour pressure at ambient temperature. In this work vapour pressure measurements are used to obtain the latent heats of sublimation for triiodophosphine and diphosphorus tetraiodide. These are then incorporated in the thermodynamic cycles (see p.200) for triiodophosphine and diphosphorus tetraiodide to obtain values for the average bond dissociation energy ($\bar{E}_{P-I}$) and the bond energy (E_{P-P}) respectively.

(2) Basic Principles - On the basis of the kinetic theory of gases Knudsen[195] proposed the following relationship between density (ρ), number of impacts (n) and the pressure (p) for an effusing gas

$$\rho = Nm \quad \text{.................} \quad (I)$$

$$n = \tfrac{1}{4}N\bar{c} \quad \text{.................} \quad (II)$$

$$p = \tfrac{1}{3}Nm\overline{c^2} \quad \text{.............} \quad (III)$$

where

N = number of molecules cm^{-3}

m = mass of substance

$\bar{c}$ = mean velocity of molecules

$\overline{c^2}$ = mean square velocity of molecules and for an equilibrium between a solid and its saturated vapour pressure the expression is derived by combining equation (I) and (II) which gives

$$\frac{W}{tA} = \frac{1}{4}\bar{c}\,(\rho - \rho') \;\ldots\ldots\ldots\ldots\; (IV)$$

where

ρ = density of the material inside the effusion cell

ρ' = density of the material outside the orifice of the cell (where if condensed immediately $\rho = 0$)

W = weight of material effused through area (A) in time (t)

While combining equations (I) and (III) with the ideal gas equation, the mean thermal molecular velocity, $\bar{c}$, is obtained which is as follows

as $p = \frac{1}{3}Nm\overline{c^2}$

and $Nm = \rho = \frac{M}{v} = \frac{M}{RT/p} = \frac{Mp}{RT}$

also $\frac{1}{3}\overline{c^2} = \frac{\pi}{8}(\bar{c})^2$ (Maxwellian law of distribution of velocities)

where

$(\bar{c})^2$ = mean velocity square of the molecules

therefore $p = \frac{\pi}{8}(\bar{c})^2 \times \frac{Mp}{RT}$

or $(\bar{c})^2 = \frac{8RT}{M\pi}$

or $$\bar{c} = \sqrt{\frac{8RT}{M\pi}} \;\ldots\ldots\ldots\ldots\; (V)$$

Also combining (IV) and (V) one arrives at

$$\frac{W}{tA} = \frac{1}{4}\sqrt{\frac{8RT}{M\pi}}\ \frac{Mp}{RT}$$

or $$p = \frac{W}{At}\sqrt{\frac{2\pi RT}{M}} \quad \ldots\ldots\ldots\ldots\ldots \text{(VI)}$$

where

p = vapour pressure (mm. Hg.)

W = weight of substance (g)

A = area of the orifice (cm^2)

t = time (sec.)

R = gas constant (erg. $deg.^{-1}$ $mole^{-1}$)

T = absolute temperature (^oK)

M = moleculer weight of substance

Also, during the effusion process some of the molecules undergo diffuse reflection with the wall of the orifice. This can be expressed as

$$\delta_o = (2 - f_o)/f_o$$

where

f_o = fraction of the molecules undergoing diffuse reflection, thus $f_o = 1$

Equation (VI) is valid under the ideal conditions of infinitely thin edges to the orifice and a large mean free path to orifice diameter ratio. In practice, neither of these conditions is exactly met and correction factors are introduced. The shape factor can be determined either by the Kundsen method (Kn) which gives

$$Kn = 1 + \frac{8r}{3L}$$

or it can be obtained empirically from Clausing, who tabulated the ratio of l/r (where l = length of orifice, r = radius of the orifice) vs. the clausing constant (Kc).

Thus the equation (VI) can be written as

$$p = \frac{W}{tA} \sqrt{\frac{2\pi RT}{M}} \times \frac{1}{Kc} \times \frac{1}{\delta o} \quad \ldots\ldots\ldots\ldots\ldots (1)$$

$$\text{or } p = \frac{W}{tA} \sqrt{\frac{2\pi RT}{M}} \times Kn \times \frac{1}{\delta o} \quad \ldots\ldots\ldots\ldots\ldots (2)$$

The values of p determined by equations (1) and (2) differ little. These equations are now extensively used[196,197] in effusion manometry. Sometimes the average value of p from these equations is used.

Recent theoretical work by Hiby and Pahl[202] has shown the importance of a correction factor (F) which takes account of the fact that, in practice, r/λ does not approach zero and hence for the transition region where r/λ is not zero a correction factor given by

$$F = \left(\frac{1}{1 + K_2\, r/2\lambda}\right) \quad \text{is applied.}$$

where

r = radius of orifice

λ = mean free path

K_2 = shape constant = 0.48

($r/2\lambda$ is a pressure sensitive term)

and hence the final equation is

$$p = \frac{W}{tA} \sqrt{\frac{2\pi RT}{M}} \left(\frac{3L + 8r}{8r}\right) \frac{1}{1+K_2 r/2\lambda} \; \frac{1}{\delta o} \ldots\ldots\ldots (3)$$

The final equation (3) is in fact equal to equation (2) x F. In all these equations the value of δo is conventionally put to unity.

(3) Design and Construction - The effusion manometer is a vacuum holding assembly embodying (i) a sample cell fabricated in an inert material in good thermal contact with the heat sink, (ii) cold-zone devices to condense the material effused, and, (iii) a heat sink.

The effusion manometer designed and constructed for this work in this laboratory is shown on pp. 105,107 This manometer is similar to that constructed by Edwards and Kington.[196] Certain modifications were introduced because of (i) the corrosive nature of the phosphorus compounds (ii) the attack on greases of all kinds by such compounds (iii) quantitative removal of a thermally-conducting grease, around the outer body of the effusion cell, has been proved to be very difficult.

In view of the above limitations, the effusion cell body was made of stainless steel and the foil of gold. The foil was kept in position by a stainless steel locking ring. The drilling of the hole in the foil was performed using a No: 80 high-speed twist drill. The burring was removed by a fine abrasive paste. The radius of the orifice was measured by a travelling microscope and planimeter on a photomicrograph (linear magnification x 100). The thickness was deduced from a knowledge of weight, density and surface area of the foil. Thermal contact of the cell with the heat sink was established via precision threading (26 t.p.i. Whitworth) into the circular copper block. The circular copper block was silver-soldered to the Kovar-to-pyrex glass seal. Complete vacuum integrating was ensured by liberal use of Torr-Seal.[206] The vacuum inside the effusion manometer (10^{-5} mm. Hg) was produced via a mercury diffusion pump backed by two-stage rotary pump. The pressure measurements were via a Pirani Gauge inserted just after the ball joint of the effusion manometer (i.e. before the liquid nitrogen trap) and also by a McLeod Gauge situated between two liquid nitrogen traps. The vapour pressure

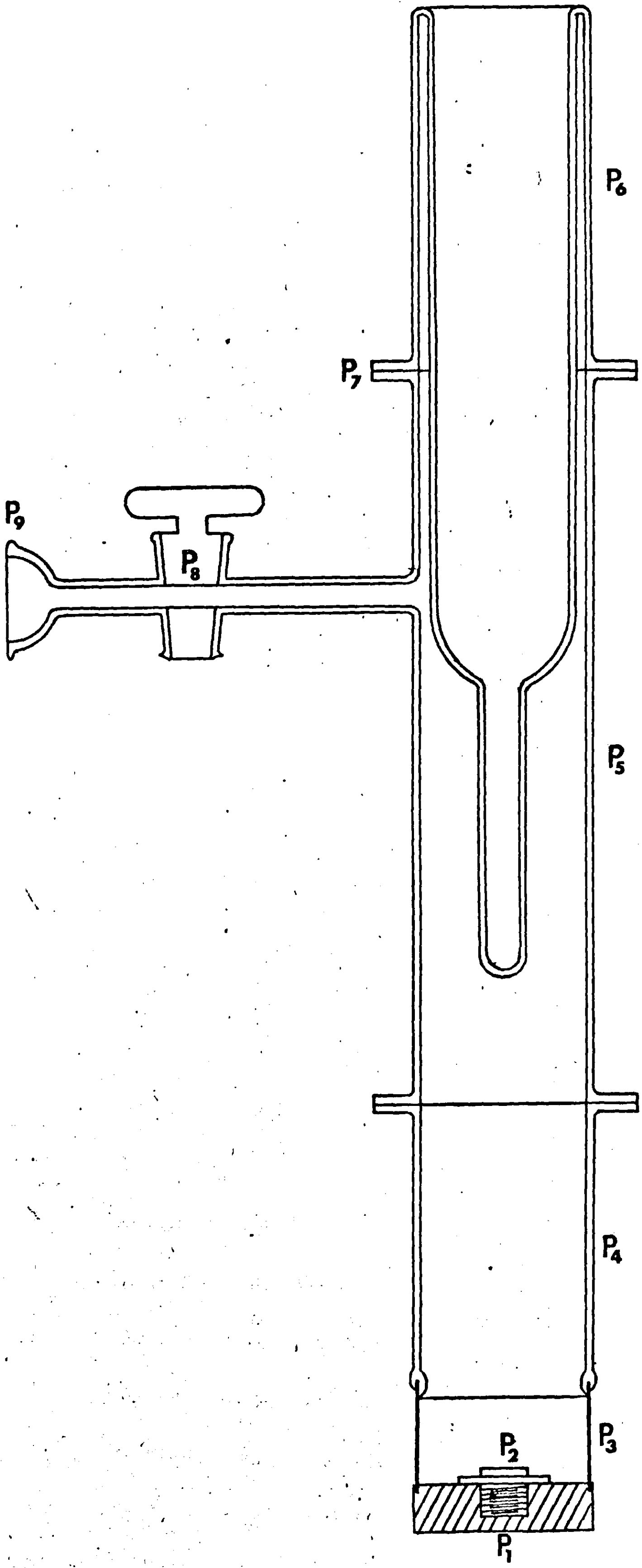


Fig. Longitudinal Section through Effusion Manometer.

(x 0.33 natural size)

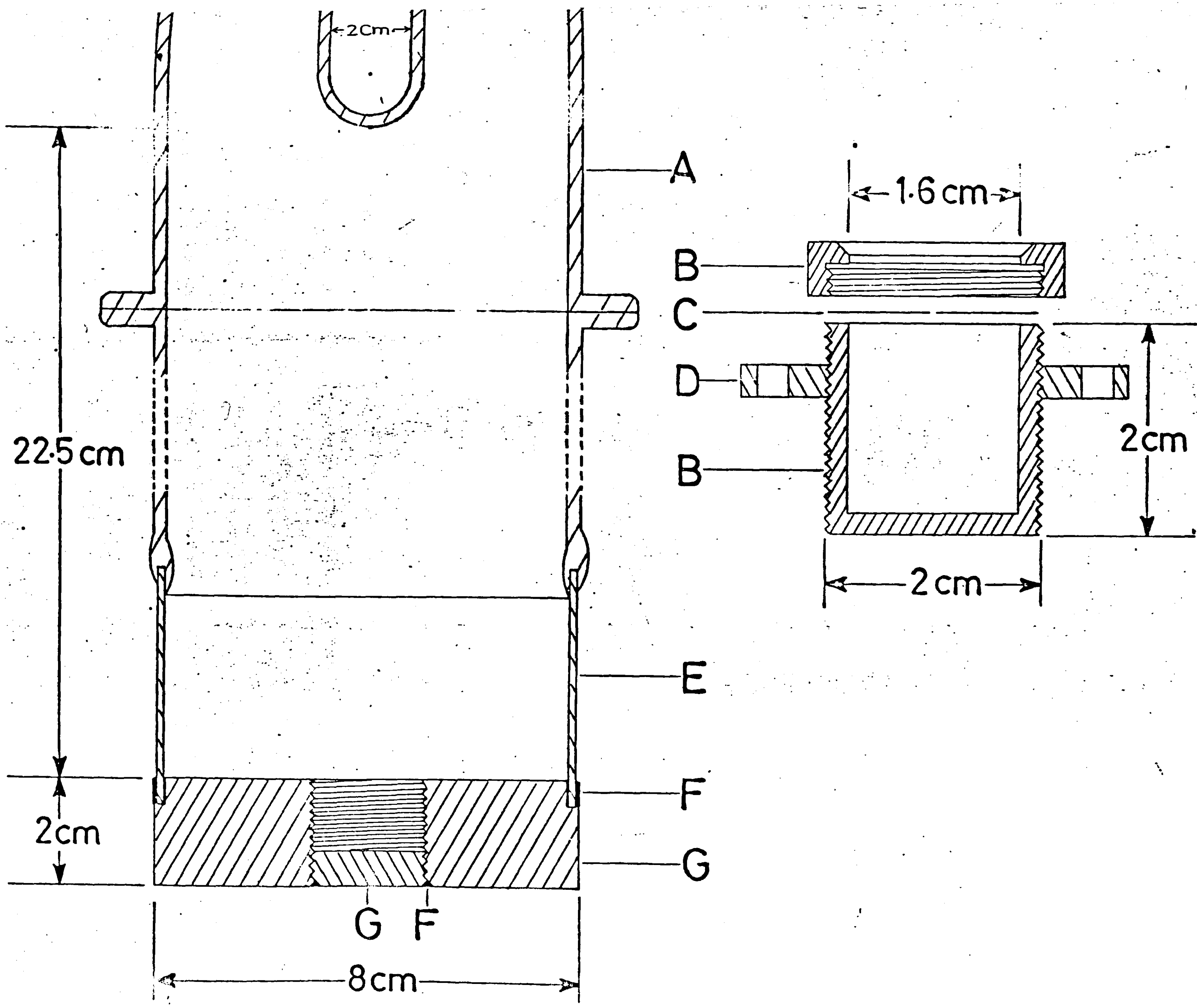
studies were performed within two distinct temperature ranges. For the temperature range of 20-28°C the thermal equilibrium of the heat sink was achieved in the water-bath controlled by Tronac thermistor regulator (PTC - 1000, Provo, UTAH) leading to a bath control of ± 0.001°C. The temperature of the bath was monitored by a Quartz thermometer (2801A, Hewlett Packard) with a resolution of ± 0.0001°C and also a mercury thermometer (N.P.L., B.S. 791 type) of accuracy ± 0.001°C. For the temperature range 50 - 80°C, the heat sink was immersed in a paraffin bath regulated by a sunvic controller (type 102/4) coupled with a Gallenkamp thermostat. The temperature of this bath was recorded to ± 0.02°C using a mercury thermometer (N.P.L. ZECOL, EDM 3319, No: 66).

The constructed effusion manometer was successfully operated up to a maximum temperature limit of 100°C and with a vacuum of 10^{-5} mm. Hg. maintained over two to three days.

<u>Longitudinal Section through Effusion Manometer (x 0.33 natural size)</u>

(P = part)

P_1	Copper block
P_2	Stainless steel cell
P_3	Kovar metal
P_4	Lower pyrex section
P_5	Central pyrex section (attached to vacuum line)
P_6	Upper pyrex section (cold finger, FGY 5 type, Quickfit)
P_7	Flanges, 2.2 cm. (Quickfit)
P_8	Tap $H_{(10)v}$ type (Jencons)
P_9	Socket joint 625 type (Quickfit)


2Cm
A
22·5 cm
1·6 cm
B
C
D
B
2cm
2 cm
E
F
2cm
G
G
F
8cm

Longitudinal Section through Effusion Manometer (natural size) and Effusion Cell (x 2 natural size)

A	Pyrex glass
B	Stainless steel
C	Gold foil
D	Duralumin yoke
E	Kovar metal
F	Silver solder
G	Copper block

(4) Operating procedure - The effusion manometer was initially operated with ferrocene as test compound. The ferrocene was twice recrystallized using a modified purification procedure of Edwards[167] et al. m.pt. 175-176°C (found) (lit.[167] m.pt. 175.5-176°C). The cell was filled to two-thirds capacity with the powdered ferrocene. The cell was inserted into heat sink for effusion over a temperature range of 20-28°C for the period of ca. 24 hr. The effused material was immediately condensed above the effusion cell by a cold finger containing acetone and carbon dioxide mixture at ca. 80°C. At the end of each run, the weight loss of the ferrocene from the cell was determined by difference. Throughout the effusion manometric work weighings to ± 0.0001 g. were made using the same Stanton electrical balance (CL 41). The handling of the cell was via a special pair of clippers and thermally insulated gloves. In the case of phosphorus compounds, a similar procedure was followed in a dry-box filled with an inert atmosphere of nitrogen. Each run, in all of these experiments, was repeated at least three times over the same temperature range.

SECTION-III. RESULTS

CHAPTER SIX: THERMOCHEMICAL RESULTS

THAM Results

The literature gives the following heats of solution of THAM in 0.1 M HCl at 25° for N (H_2O : THAM) = 500 to 2000. In this work the range 728-779 for the C.T.E. calorimeter and 964-1058 for adiabatic calorimeter was used.

TABLE Some literature heats of neutralization for THAM

$-\Delta H$ (Kcal $mole^{-1}$)	$-\Delta H$ (KJ $mole^{-1}$)	Reference	
7.107 ± 0.001	29.736	Gunn[207]	1965
7.111 ± 0.001	29.752	Sunner[208] and Wadsö	1966
7.112 ± 0.002	29.757	Öjeland[209] and Wadsö	1967
7.109 ± 0.001	29.744	Hill,[177] OJeland and Wadso	1969
7.155 ± 0.002	29.936	This Work	

TABLE Heat of neutralization of THAM* in 0.1 M HCl (150 ml.) at 25° using C.T.E. Calorimeter

$(HOCH_2)_3CNH_2$(cryst.) + HCl H_2O (liq.) = $[(HOCH_2)_3C\overset{+}{N}H_3Cl^-]\,nH_2O$

Wt. THAM (g)	$N^{\ddagger}$	ΔHobs KJ $mole^{-1}$	ΔHobs Kcal $mole^{-1}$
1.3858	728	-29.99	-7.17
1.3000	777	-29.83	-7.13
1.3256	762	-31.00	-7.41
1.3836	730	-30.67	-7.33
1.3480	749	-29.75	-7.11
1.3791	732	-29.91	-7.15
1.3142	768	-30.42	-7.28
1.2663	797	-29.50	-7.05
1.3243	762	-30.08	-7.19
1.3228	763	-29.75	-7.11
1.3778	768	-29.66	-7.09
1.3185	766	-30.04	-7.18
1.3175	766	-29.91	-7.15
1.3264	761	-29.66	-7.09
1.3506	747	-29.54	-7.06
1.3207	764	-29.75	-7.11
1.2949	780	-29.96	-7.16
1.3177	766	-29.83	-7.13
1.3188	765	-29.99	-7.17
1.3743	735	-29.87	-7.144

*Tris(hydroxymethyl)aminomethane

$N^{\ddagger}$ is mole ratio of water to THAM

25°C = 298.15°K

TABLE Heat of neutralization of THAM* in 0.1 M HCl (200 ml.) at 25° using Adiabatic Calorimeter

Wt. THAM (g)	N‡	ΔHobs KJ mole^{-1}	ΔHobs Kcal mole^{-1}
1.3900	963	29.83	-7.13
1.3954	965	29.87	-7.14
1.2721	1058	29.83	-7.13
1.3201	1020	29.91	-7.155

*Tris(hydroxymethyl)aminomethane

N‡ is mole ratio of water to THAM

Details of a typical C.T.E. run:

Thermistor F53 Type

(I) EXPERIMENT: $\Delta Hr\ H_2NC(CH_2OH)_3$(THAM)

4025.5 Ω 25°

REACTION		TIME(MIN)		CALIBRATION
4024.7		0		4034.1
4024.8		½		4034.0
4024.9		1		4034.0
4025.0		1½		4033.9
4025.1		2		4033.8
4025.2	FORE-RUN	2½	FORE-RUN	4033.8
4025.3		3		4033.7
4025.4		3½		4033.6
4025.5		4		4033.5
4025.6		4½		4033.4
4025.7		5*		4033.3
3957.7		5½		4023.2
3958.5		6		4007.2
3959.0		6½	HEATER TIME	3991.2
3959.6		7	(160.10 sec.)	3975.3
3960.1		7½		3960.3
3960.6		8		3950.0
3961.1		8½		3949.1
3961.7		9		3949.5
3962.2		9½		3950.0
3962.7		10		3950.6
3963.4		10½		3951.1

*ampoule fracture at 5 min.

3963.8		11		3951.7
3964.3	AFT-RUN	11½	AFT-RUN	3952.2
3964.8		12		3952.8
3965.3		12½		3953.3
3965.8		13		3953.9
3966.3		13½		3954.6
3966.6		14		3955.1
3967.0		14½		3955.7
3967.4		15		3956.3
3967.9		15½		3957.1
3968.3		16		3957.7
3968.7		16½		3958.3
3969.1		17		3958.9
3969.5		17½		3959.3
3970.0		18		3959.8
3970.4		18½		3960.2
3970.8		19		3960.6
3971.2		19½		3961.4
3971.6		20		3962.0

(II) <u>OBSERVATIONS:</u>

REACTION TEMP = 25.00 ± 0.01°C.

HEATER TIME = 160.10 sec.

Wt. REACTANT = 1.3743 Tri(hydroxymethyl)aminomethane (THAM)

Mol. Wt. REACTANT = 121.14

Vol. SOLVENT = 0.1 N HCl (150 ml.)

N = moles (solvent/reactant) = 735

R_1 = 4025.8 ohms, log R_1 = 3.60485220

R_2 = 3958.8 ("), log R_2 = 3.59756356

Difference = 67.0 Ω, ΔTr^* = 0.00728864

R_3 = 4033.2 ("), log R_3 = 3.60564976

R_4 = 3947.5 ("), log R_4 = 3.59632214

Difference = 85.7 Ω, ΔTc^* = 0.00932762

V_s = 0.5740 Volts

V_1 = 0.4800 Volts

$P = 11V_1 X(V_s - V_1/10)$ = 2.7772 Watts

R_H(calc.) $= 11V_1/(V_s - V_1/10)$ = 10.038 ohms

$$f = \frac{R_H \text{ (actual)}}{R_H \text{ (calc.)}} = 9.800/10.038 = 0.9762$$

(III) <u>CALCULATIONS:</u>

$$\Delta H = \frac{f \times P}{4184} \times \frac{M}{w} \times t \times \frac{\Delta Tr}{\Delta Tc}$$

(IV) <u>RESULT:</u> <u>7.14 kcal/mole</u>

[*] This is not precisely the numerical temperature but rather a function directly proportional to it (see p. 76).

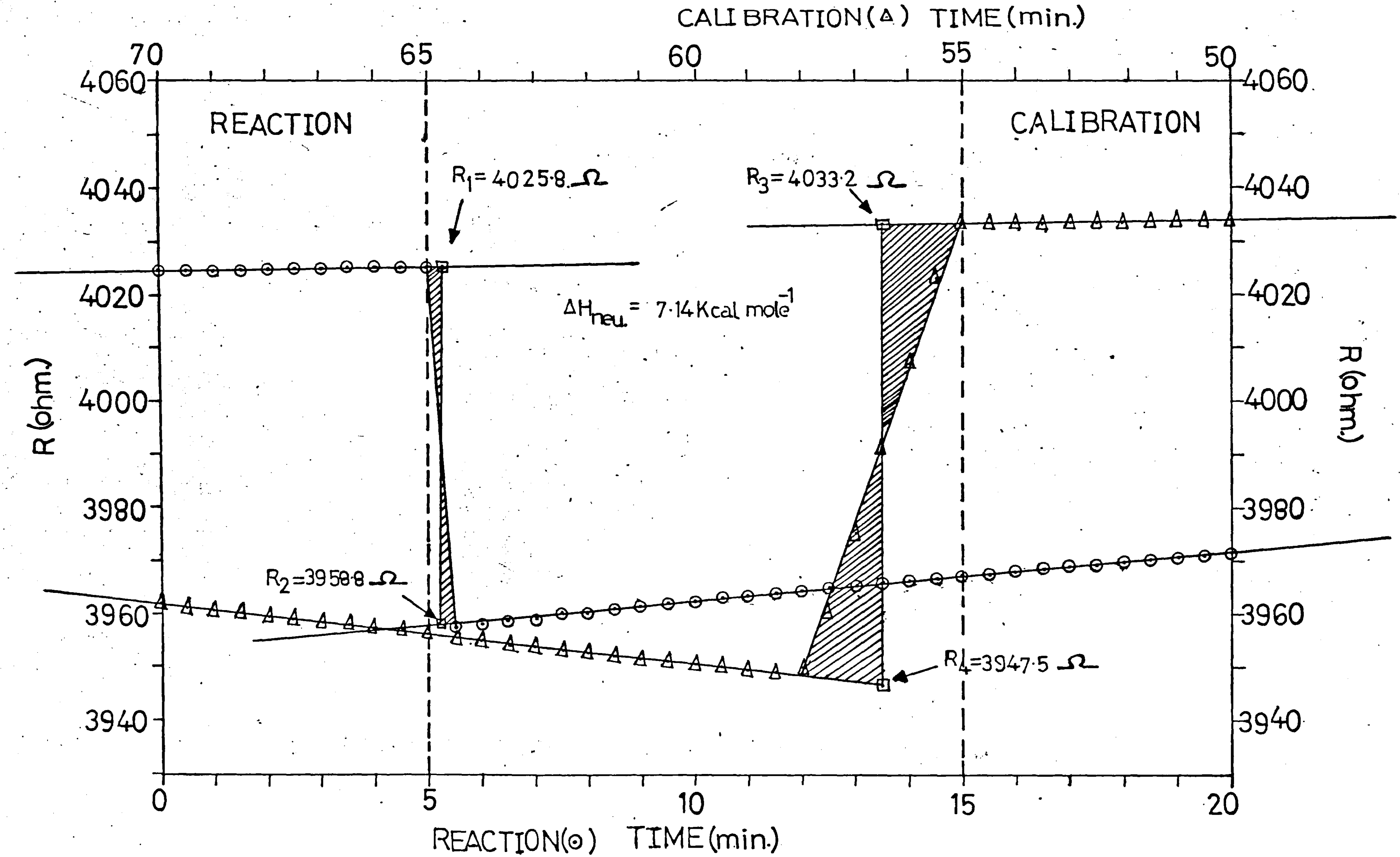


Fig. Typical Constant Temperature Environment Calorimeter Run for THAM.

Details of a typical adiabatic run:

Thermistor F53 Type

(I) EXPERIMENT: ΔH_r $H_2NC(CH_2OH)_3$ (THAM)

4609.0 Ω 25°

REACTION		TIME(MIN)		CALIBRATION
4610.5		0		4610.7
4610.4		1		4610.6
4610.3		2		4610.5
4610.2		3		4610.4
4610.2		4		4610.3
4610.1	FORE-RUN	5	FORE-RUN	4610.2
4610.1		6		4610.0
4610.0		7		4609.9
4609.9		8		4609.8
4609.9		9		4609.7
4609.9		10*		4609.5
4550.8		11		4599.5
4550.8		12	HEATER TIME	4585.5
4550.8		13	(236.72 sec.)	4871.5
4550.9		14		4558.5
4550.9		15		4552.1
4550.9		16		4551.7
4550.9		17		4551.5
4550.9		18		4551.5
4550.8		19		4551.4
4550.7		20		4551.4
4550.6		21		4551.3

*ampoule fracture at 10 min.

4550.5		22		4551.2
4550.5		23		4551.1
4550.4	AFT-RUN	24	AFT-RUN	4551.0
4550.3		25		4550.9
4550.2		26		4550.8
4550.1		27		4550.7
4550.0		28		4550.6
4549.9		29		4550.5
4549.8		30		4550.4
4549.7		31		4550.3
4549.5		32		4550.1
4549.5		33		4550.0
4549.4		34		4549.9
4549.2		35		4549.8
4549.1		36		4549.7
4548.8		37		4549.6
4548.6		38		4549.5
4548.4		39		4549.4
4548.1		40		4549.3

(II) OBSERVATIONS:

REACTION TEMP = 25.00 ± 0.01°C

HEATER TIME = 236.72 sec.

Wt. REACTANT = 1.3201 g. Trishydroxymethylaminomethane (THAM)

Mol. Wt. REACTANT = 121.14

Vol. SOLVENT = 0.1 N HCl (200 ml)

N = moles (solvent/reactant) = 1020

R_1 = 4609.9 ohms, log R_1 = 3.66369150

R_2 = 4551.6 ("), log R_2 = 3.65816409

Difference 58.3 Ω, Tr* = 0.00552741

R_3 = 4609.5 ("), log R_3 = 66365382

R_4 = 4552.4 ("), log R_4 = 65824041

Difference 57.1 Ω, Tc* = .00541341

$V_H = 10V_1 + P_2 - P_1 = 4.5894$

$V_1 = 0.4203$ volts

$V_2 = 0.3356$ volts

$P_1 = 0.0161$ volts

$P_2 = 0.4025$ volts

$I = \frac{Vs}{Rs} - \frac{V_1}{10} = 0.29417$

$R_s = 0.9982$ ohm.

$R_H = \frac{V_H}{I} = 15.601$ ohm.

$P = V_H \times I$

(III) CALCULATIONS:

$$\Delta H = \frac{P}{4184} \times \frac{M}{w} \times t \times \frac{\Delta Tr}{\Delta Tc}$$

(IV) RESULT: 7.15 kcal/mole

*This is not precisely the numerical temperature but rather a function directly proportional to it (see p.76)

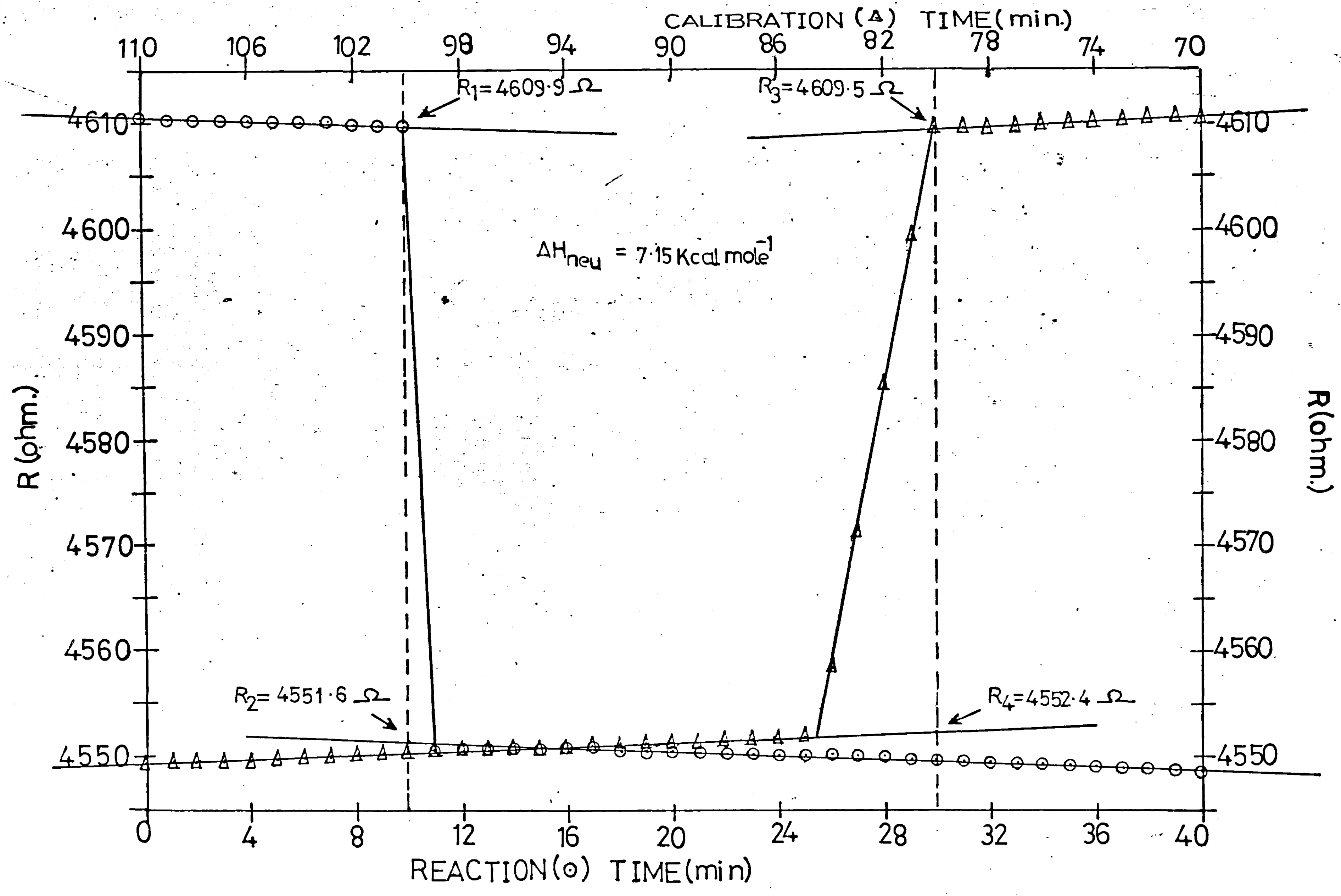
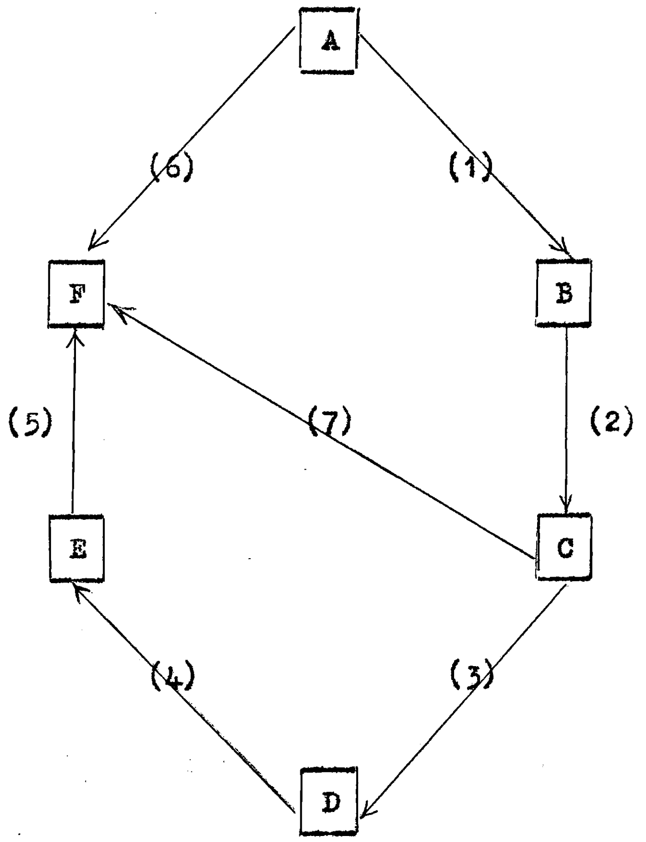


Fig. Typical Adiabatic Calorimeter Run for THAM.

Thermodynamic Cycle for Pentaphenylcyclopentaphosphine



Legend

A = $(C_6H_5P)_5$ (cryst.)

B = $C_6H_5PBr_2$ (in C_6H_6)

C = $C_6H_5PBr_2$ (liq.)

D = $C_6H_5PO_2H_2$ (aq.)

E = $C_6H_5PO_2H_2$ (cryst.)

F = $C_6H_5PO_3H_2$ (aq.)

(1) = Br_2 (in C_6H_6)

(2) = C_6H_6

(3), (4) = H_2O

(5), (6), (7) = Br_2 (aq.)

The following detailed reactions refer to the generalized thermodynamic cycle for pentaphenylcyclopentaphosphine. (All steps at 25°C). Heats of mixing of the products were ignored.

Step (1) The oxidation of pentaphenylcyclopentaphosphine with benzene solution of bromine

$$\frac{1}{5}(C_6H_5P)_5 \text{ (cryst.)} + Br_2 \text{ (in } C_6H_6) = C_6H_5PBr_2 \text{ (in } C_6H_6) \text{ \_\_\_\_\_\_\_\_ } \Delta H_1$$

$$\Delta H_1 = \Delta H^o_f\,[C_6H_5PBr_2 \text{ in } C_6H_6] - \frac{1}{5}\Delta H^o_f[(C_6H_5P)_5, \text{ cryst.}] - \Delta H^o_f\,(Br_2 \text{ in } C_6H_6)$$

The stoichiometry of this bromination is described on P.133

Step (2) The solution of phenyldibromophosphine in benzene

$$C_6H_5PBr_2 \text{ (liq.)} + C_6H_6 \text{ (liq.)} = C_6H_5PBr_2 \text{ (in } C_6H_6) \text{ \_\_\_\_\_\_\_\_ } \Delta H_2$$

$$\Delta H_2 = \Delta H^o_f\,(C_6H_5PBr_2 \text{ in } C_6H_6) - \Delta H^o_f\,(C_6H_5PBr_2, \text{ liq.})$$

Step (3) Hydrolysis of phenyldibromophosphine

$$C_6H_5PBr_2 \text{ (liq.)} + 2H_2O \text{ (liq.)} = (C_6H_5PO_2H_2 + 2HBr) \text{ aq. \_\_\_\_\_\_\_\_ } \Delta H_3$$

$$\Delta H_3 = \Delta H^o_f\,[C_6H_5PO_2H_2, \text{ aq.}] + 2\Delta H^o_f[HBr, \text{ aq.}] - 2\Delta H^o_f[H_2O, \text{ liq.}] - \Delta H^o_f[C_6H_5PBr_2, \text{ liq.}]$$

Step (4) The solution of phenylphosphonous acid

$$C_6H_5PO_2H_2 \text{ (cryst.)} + H_2O \text{ (liq.)} = (C_6H_5PO_2H_2) \text{ aq. \_\_\_\_\_\_\_\_ } \Delta H_4$$

$$\Delta H_4 = \Delta H^o_f\,[C_6H_5PO_2H_2, \text{ aq.}] - \Delta H^o_f\,[C_6H_5PO_2H_2, \text{ cryst.}]$$

Step (5) Oxidation of phenylphosphonous acid

$$C_6H_5PO_2H_2\ (\text{cryst.}) + (Br_2 + H_2O)\ \text{aq.} = (C_6H_5PO_3H_2 + 2HBr)\ \text{aq.} \ \rule{4em}{0.4pt}\ \Delta H_5$$

$$\Delta H_5 = \Delta H^o_f\,[C_6H_5PO_3H_2,\ \text{aq.}] + 2\Delta H^o_f\,(HBr,\ \text{aq.}) - \Delta H^o_f\,[C_6H_5PO_2H_2,\ \text{cryst.}] - \Delta H^o_f\,(Br_2,\ \text{aq.}] - \Delta H^o_f\,(H_2O,\ \text{liq.}]$$

Step (6) Oxidation of pentaphenylcyclopentaphosphine

$$\frac{1}{5}(C_6H_5P)_5\ (\text{cryst.}) + (2Br_2 + 3H_2O)\ \text{aq.} = [C_6H_5PO_3H_2 + 4HBr]\ \text{aq.} \ \rule{4em}{0.4pt}\ \Delta H_6$$

$$\Delta H_6 = \Delta H^o_f\,[C_6H_5PO_3H_2,\ \text{aq.}] + 4\,\Delta H^o_f\,(HBr,\ \text{aq.}] - \frac{1}{5}\overset{\Delta H^o_f}{[}(C_6H_5P)_5,\ \text{cryst.}) - 2\Delta H^o_f\,(Br_2,\ \text{aq.}) - 3\,\Delta H^o_f\,[H_2O,\ \text{liq.}]$$

Summing up the equations for ΔH_1 to ΔH_6, one obtains,

$$\sum_{1}^{5}\Delta H_i - \Delta H_6 = \Delta H^o_f\,(Br_2,\ \text{aq.}] - \Delta H^o_f\,(Br_2 \text{ in } C_6H_6]$$

Step (7) Oxidation of phenyldibromophosphine

$$C_6H_5PBr_2\ (\text{liq.}) + [Br_2 + 3H_2O)\ \text{aq.} = (C_6H_5PO_3H_2 + 4HBr)\ \text{aq.} \ \rule{4em}{0.4pt}\ \Delta H_7$$

$$\Delta H_7 = \Delta H^o_f\,[C_6H_5PO_3H_2,\ \text{aq.}] + 4\,\Delta H^o_f\,[HBr,\ \text{aq.}) - \Delta H^o_f\,[C_6H_5PBr_2,\ \text{liq.}] - \Delta H^o_f\,[Br_2,\ \text{aq.}] - 3\,\Delta H^o_f\,[H_2O,\ \text{liq.}]$$

$$\therefore\ \Delta H_7 = \Delta H_3 + \Delta H_4 + \Delta H_5$$

Results for the cycle $((C_6H_5P)_5)$

The experimental values at 25°C for individual steps in the cycle for pentaphenylcyclopentaphosphine are as follows:-

				K cal mole^{-1}
Step (1)	ΔH_{obs}	=	-28.64 ± 0.35	(This work)
Step (2)	ΔH_{obs}	=	0.58 ± 0.01	(This work)
Step (3)	ΔH_{obs}	=	-41.7 ± 0.08	(lit.[139] and confirmed)
Step (4)	ΔH_{obs}	=	-1.43 ± 0.04	(lit.[139] and confirmed)
Step (5)	ΔH_{obs}	=	-61.31 ± 0.33	(This work)
Step (6)	ΔH_{obs}	=	-133.48 ± 0.32	(This work)
Step (7)	ΔH_{obs}	=	-104.36 ± 0.13	(This work)

From the equations of the generalized thermodynamic cycle it can be seen that

$$\Delta H_6 - \sum_{1}^{5} \Delta H_i = \Delta H^o_f \, [Br_2, aq.] - \Delta H^o_f \, [Br_2, C_6H_6]$$

It can be seen from the measured data above, that the LHS of this equation equals to -0.98 ± 0.58 K cal. The heat of solution of Br_2 in C_6H_6 is reported on P. 130 as -1.44 ± 0.02 K cal and the corresponding value for H_2O is known -0.62 K cal.[210] Thus the RHS equals 0.82 K cal.; hence the discrepancy is 1.80 K cal.

Also comparison of the value obtained from ΔH_7 (i.e. -104.36 ± 0.13 K cal) with that of the sum of $\Delta H_3 + \Delta H_4 + \Delta H_5$ (i.e. -104.44 ± 0.34 K cal), shows consistency in this section of the cycle. Therefore the discrepancy mentioned above of 1.80 K cal must be attributed to reactions 1, 2 or 6 (probably 6).

TABLE C.T.E. Calorimetric Results for Step No: (1) in Thermodynamic cycle for Pentaphenylcyclopentaphosphine referring to the following reaction in benzene (125 ml.) at 25°C. $N(\phi H:Br_2)$ = 511-1075

$$(\phi P)_5\ (\text{cryst.}) + 5\ Br_2\ (\text{in}\ \phi H) = 5\ PBr_2\ (\text{in}\ \phi H)$$

$\Phi = C_6H_5$

Wt. $(\phi P)_5$ (g)	Bromine required (g)	Bromine used (g)	% (Excess)	$N(\phi H: P)$	ΔHobs. KJ mole^{-1}	ΔHobs. Kcal mole^{-1}
0.3067	0.4543	0.4685	3.12	565	-127.57	-30.49
0.3077	0.4781	0.4982	4.20	563	-124.05	-29.65
0.3003	0.4448	0.4769	7.21	577	-117.95	-28.19
0.1504	0.2280	0.2385	4.60	1151	-117.28	-28.03
0.1573	0.2330	0.2385	2.36	1100	-124.18	-29.68
0.1483	0.2196	0.2385	8.60	1167	-111.38	-26.62
0.1480	0.2192	0.2385	8.80	1170	-116.02	-27.73
0.1513	0.2225	0.2385	7.19	1144	-120.04	-28.69
0.1512	0.2225	0.2385	7.19	1145	-119.95	-28.67
0.3000	0.4558	0.50138	10.00	577	-120.04	-28.69

Av. ΔHobs = -119.83 ± 1.46 KJ mole^{-1}

= -28.64 ± 0.35 Kcal mole^{-1}

(1) Complete thermodynamic cycle for pentaphenycyclopentaphosphine is shown on P. 208

(2) The stoichiometry of the reaction under calorimetric conditions was established in various steps of the cycle.

25°C = 298.15°K, Av = Average, Obs = observed

TABLE C.T.E. Calorimetric Results for Step No: (2) in Thermodynamic cycle for Pentaphenylcyclopentaphosphine referring to the following reaction in benzene (125 ml.) at 25°C

$$\phi PBr_2\ (liq.) + \phi H\ (liq.) = \phi PBr_2\ (in\ \phi H)$$

Wt. ϕPBr_2 (g)	(ϕH: ϕPBr_2)	ΔHobs. KJ mole^{-1}	ΔHobs. Kcal mole^{-1}
0.3644	1179	2.38	0.57
0.5400	795	2.43	0.58
0.5337	805	2.43	0.58
0.4892	878	2.30	0.55
0.7048	609	2.72	0.65
0.6628	648	2.22	0.53

Av. ΔHobs. = 2.43 ± 0.04 KJ mole^{-1}

= 0.58 ± 0.01 Kcal mole^{-1}

Calorimetric values for step No: (3) and No: (4) stated in thermodynamic cycle for pentaphenylcyclopentaphosphine are from lit.[139] which has been confirmed here.

TABLE C.T.E. Calorimetric Results for step No: (5) in Thermodynamic cycle for Pentaphenylcyclopentaphosphine referring to the following reaction in aq. Bromine (125 ml.) at 25°C. $N(H_2O:Br_2) = 2645$

$$\phi PO_2H_2 \text{ (cryst.)} + (2Br_2 + H_2O) \text{ (aq.)} = (\phi PO_3H_2 + 4HBr) \text{ (aq.)}$$

Wt. ϕPO_2H_2 (g)	Bromine required (g)	$N(H_2O:\phi PO_2H_2)$	% (Excess) Bromine used	ΔHobs. KJ mole^{-1}	ΔHobs. Kcal mole^{-1}
0.3552	0.3995	2776	5.13	-253.21	-60.52
0.3554	0.3997	2774	5.08	-258.78	-61.85
0.3550	0.3993	2777	5.18	-255.55	-61.08
0.3545	0.3987	2782	12.46	-250.16	-59.79
0.1758	0.1977	5609	6.22	-257.90	-61.64
0.2063	0.2320	4780	3.45	-259.53	-62.03
0.1761	0.1980	5599	6.06	-260.04	-62.23

Av. ΔHobs = -256.52 ± 1.38 KJ mole^{-1}

= -61.31 ± 0.33 Kcal mole^{-1}

TABLE Adiabatic calorimetric Results for Step No: (6) in Thermodynamic cycle for Pentaphenylcyclopentaphosphine referring to the following reaction in aq. Bromine (200 ml.) at 25° $N(H_2O:Br_2) = 2383$

$$(C_6H_5P)_5 \text{ (cryst.)} + (2Br_2 + 3H_2O) \text{ (aq.)} = (C_6H_5PO_3H_2 + 4HBr) \text{ aq.}$$

Wt. $(C_6H_5)_5$ (g)	Bromine required (g)	$N(H_2O:C_6H_5P)$	% (Excess) Bromine used	ΔHobs. KJ mole^{-1}	ΔHobs. Kcal mole^{-1}
0.2307	0.6822	5205	9.35	-559.82	-133.80
0.2304	0.6813	5212	9.49	-553.50	-132.29
0.2300	0.6802	5221	9.67	-561.11	-134.11
0.2302	0.6807	5216	9.59	-560.07	-133.86
0.2305	0.6816	5210	9.44	-557.94	-133.35

Av. ΔHobs. = -558.48 ± 1.34 KJ mole^{-1}

= -133.48 ± 0.32 Kcal mole^{-1}

(1) The length of the main period was ca. 30 min. and readings were continued for further 120 min. The fore-run period was 10 min.

TABLE C.T.E. Calorimetric Results for step No: (7) in Thermodynamic cycle for Pentaphenylcyclopentaphosphine referring to the following reaction in aq. Bromine (125 ml.) at 25°C. $N(H_2O:Br_2)$ = 3351-4171

$C_6H_5PBr_2$ (liq.) + (Br_2 + $3H_2O$) (aq.) = ($C_6H_5PO_3H_2$ + 4HBr) (aq.)

Wt. $C_6H_5PBr_2$ (g)	Bromine required (g)	$N(H_2O: C_6H_5PBr_2)$	% (Excess) Bromine used	ΔHobs. KJ mole^{-1}	ΔHobs. Kcal mole^{-1}
0.5200	0.3101	3579	6.90	-436.56	-104.34
0.4335	0.2586	4293	3.01	-435.18	-104.01
0.5118	0.3053	3636	8.58	-437.52	-104.57
0.4308	0.2570	4320	3.65	-437.35	-104.53

Av. ΔHobs. = -436.64 ± 0.54 KJ mole^{-1}
= -104.36 ± 0.13 Kcal mole^{-1}

TABLE C.T.E. Calorimetric Results for the Heat of Solution of Bromine in Benzene (100 and 200 ml.)

Wt. Bromine (g)	$N(C_6H_5:Br_2)$	ΔHobs. KJ mole^{-1}	ΔHobs. Kcal mole^{-1}
0.3789	541	-6.15	-1.47
0.7456	550	-5.90	-1.41
0.7674	535	-6.07	-1.45
0.7320	560	-6.02	-1.44
0.7513	546	-5.98	-1.43

Av. ΔHobs. = -6.02 ± 0.08 KJ mole^{-1}

= -1.44 ± 0.02 Kcal mole^{-1}

TABLE C.T.E. Calorimetric Results for Heat of Solution of Tetrahydrofuran in aq. Bromine (125 ml.) at 25°C. $N(H_2O:Br_2) = 2222$

Wt. THF (g)	$N(H_2O:THF)$	ΔHobs. KJ $mole^{-1}$	ΔHobs. Kcal $mole^{-1}$
1.0105	495	-16.44	-3.93
0.8544	585	-13.81	-3.30
0.8550	584	-14.06	-3.36
1.0100	495	-16.48	-3.94
0.9961	502	-15.15	-3.62
0.8777	570	-14.85	-3.55

$$\Delta \text{Hobs.} = 15.15 \pm 0.46 \text{ KJ mole}^{-1}$$

$$= 3.62 \pm 0.11 \text{ Kcal mole}^{-1}$$

This heat of solution was the part of the four step procedure drawn for attempted concordant reaction for $(C_6H_5P)_5$ to enhance the speed of reaction but with little success.

TABLE Adiabatic Calorimetric Results for Polymeric Phenylphosphine (so called) referring to the following reaction in Benzene (200 ml.) at 25°C. $N(C_6H_5H:Br_2) = 319$

$$\frac{1}{n}(C_6H_5P)_n\ (\text{cryst.}) + 2Br_2\ (\text{in } C_6H_5H) = (C_6H_5PBr_4)\ (\text{in } C_6H_5H)$$

Wt. $(C_6H_5)_n$ (g)	Wt. Bromine required (g)	$N(C_6H_5H): C_6H_5P)$	% (Excess)	ΔHobs. KJ mole^{-1}	ΔHobs. Kcal mole^{-1}
0.1094	0.3235	2531	297.77	-205.18	-49.04
0.1050	0.3105	2633	314.04	-186.94	-44.68
0.1100	0.3253	2517	295.20	-194.72	-46.54
0.1047	0.3096	2645	315.24	-198.61	-47.47
0.1123	0.3321	2466	287.11	-200.25	-47.86
0.1092	0.3229	2536	298.14	-204.64	-48.91
0.1102	0.3259	2513	294.47	-196.86	-47.05
0.1046	0.3093	2647	315.64	-198.15	-47.36
0.1076	0.3182	2573	304.02	-199.49	-47.68

$$\text{Av. } \Delta\text{Hobs.} = -198.32 \pm 1.80 \text{ KJ mole}^{-1}\ (C_6H_5P)$$
$$= -47.40 \pm 0.43 \text{ Kcal mole}^{-1}\ (C_6H_5P)$$

(1) This was slow reaction, fore-run 10 min., main reaction period of 35 min. and aft-run readings were recorded up to 180 min.

(2) Reaction based on $C_6H_5PBr_2$ was attempted with no success.

(3) Calorimetric reaction based on $C_6H_5PBr_4$ was further subjected for bromide content analysis by conventional titrimetry and gave the expected results $C_6H_5PBr_4 + 3H_2O = C_6H_5PO_3H_2 + 4HBr$.

The establishment of the stoichiometry of the bromination of (i) pentaphenylcyclopentaphosphine and (ii) polymeric phenylphosphine

(i) Bromination of $(C_6H_5P)_5$ was based on the following reactions in benzene solution at room temperature:

$$\frac{1}{5}\ (C_6H_5P)_5 + Br_2 = C_6H_5PBr_2$$

$$\frac{1}{5}\ (C_6H_5P)_5 + 2Br_2 = C_6H_5PBr_4$$

Pentaphenylcyclopentaphosphine and bromine (5-10% excess, based on the formation of phenyldibromophosphine) were separately dissolved in benzene and the solutions mixed in a separating funnel. Initially a yellow precipitate appeared but on vigorous shaking it dissolved and a clear solution was obtained. On hydrolysis two distinct layers were obtained. The upper, (benzene), layer was separated and washed thrice, after which the washings were bromide-free. The aqueous fractions were collected and analysed for bromide by argentimetric titration. The bromide analysis indicated that quantitative formation of the phenyldibromophosphine occurred under these conditions.

This procedure was repeated using a slight excess of bromine (5-10%), based on the formation of phenyltetrabromophosphorane. In this case the bromide recovery indicated ca. 50% phenyltetrabromophosphorane formation up to the time of the extraction. Further washings gave another 10% of phenyltetrabromophosphine. Leaving the reaction mixture at room temperature for 24 hr. gave quantitative conversion to phenyltetrabromophosphorane. Thus it appears that conversion to phenyltetrabromophosphorane is slow compared with phenyldibromophosphine. Therefore the calorimetric reaction was based on phenyldibromophosphine (see thermochemical results p. 125).

(ii) Bromination of $(C_6H_5P)_n$ was based on the following reactions in benzene:

$$\frac{1}{n}\ (C_6H_5P)_n\ \text{(suspension)} + Br_2 = C_6H_5PBr_2$$

$$\frac{1}{n}\ (C_6H_5P)_n\ \text{(suspension)} + 2Br_2 = C_6H_5PBr_4$$

A similar procedure for the determination of bromide content was adopted as mentioned above for pentaphenylcyclopentaphosphine.

The reaction based on phenyldibromophosphine using 5-7% excess bromine did not seem to proceed, even after repeated attempts. The reaction based on phenyltetrabromophosphine using ca. 200% excess bromine was relatively slow in excess of bromine but went to completion, as was evident from the quantitative recovery of bromide content, after several hours.

For calorimetry, an excess of ca. 300% bromine was used, when the reaction period was ca. 30 min. (see thermochemical results p. 132).

Establishment of the stoichiometry of the oxidation of phenylphosphonous acid with aqueous bromine

This was based on the following reaction.

$$C_6H_5PO_2H_2 + Br_2 + H_2O = C_6H_5PO_3H_2 + 2HBr$$

It is possible that the above equilibrium lies appreciably to the left.

Phenylphosphonous acid was allowed to react with excess bromine (5-10%) and the resulting solution was analysed for bromine by an iodometric method. Bromine recovery indicated 100% reaction within 15 min. at room temperature.

TABLE C.T.E. Calorimetric Results for Tricyanophosphine referring to the following reaction in water (200 ml.) at 25°C.

$$P(CN)_3 \text{ (cryst.)} + 3H_2O \text{ (liq.)} + (H_3PO_3 + 3HCN) \text{ (sol.)}$$

Wt. $P(CN)_3$ (g)	$N(H_2O:P(CN)_3)$	ΔHobs. KJ $mole^{-1}$	ΔHobs. Kcal mol^{-1}
0.2491	4862	-207.86	-49.68
0.1898	6381	-207.15	-49.51
0.2055	5894	-207.15	-49.51
0.2599	4660	-206.02	-49.24
0.2444	4955	-209.78	-50.14
0.2500	4845	-206.69	-49.40

$$\text{Av. } \Delta\text{Hobs.} = -207.44 \pm 0.50 \text{ KJ mole}^{-1}$$
$$= -49.58 \pm 0.12 \text{ Kcal mole}^{-1}$$

(1) $P(CN)_3$ thrice sublimed used for this purpose

(2) Purity checked by microanalysis and potentiometric titrations

TABLE C.T.E. Calorimetric Results for Tri(isocyanato)phosphine referring to the following reaction in water (200 ml.) at 25°C.

$$P(NCO)_3\ (liq.) + 3H_2O\ (liq.) = (3HNCO + H_3PO_3)\ (sol.)$$

Wt. $P(NCO)_3$ (g)	$N(H_2O:P(NCO)_3)$	ΔHobs. KJ $mole^{-1}$	ΔHobs. Kcal $mole^{-1}$
0.1747	9984	-333.63	-79.74
0.1950	8946	-334.47	-79.94
0.1737	10000	-333.33	-79.67
0.2140	8169	-331.92	-79.33
0.3580	4873	-331.96	-79.34
0.1883	9263	-334.26	-79.89
0.4266	4089	-334.93	-80.05
0.3562	4898	-336.73	-80.48

$$\text{Av. } \Delta H\text{obs.} = -333.92 \pm 1.30 \text{ KJ mole}^{-1}$$
$$= -79.81 \pm 0.31 \text{ Kcal mole}^{-1}$$

(1) $P(NCO)_3$ freshly distilled was used for the calorimetric run. The run was conducted within 1 hr. of distillation.

TABLE C.T.E. Calorimetric Results for Phenyltetrabromophosphorane referring to the following reaction in water (125 ml.) at 25°C

$$C_6H_5PBr_4 \text{ (cryst.)} + 3H_2O \text{ (liq.)} = (C_6H_5PO_3H_2 + 4HBr) \text{ (sol.)}$$

Wt. $C_6H_5PBr_4$ (g)	$N(H_2O:C_6H_5PBr_4)$	ΔHobs. KJ mole^{-1}	ΔHobs. Kcal mole^{-1}
0.1372	21667	-334.01	-79.83
0.2711	10963	-342.50	-81.86
0.2442	12171	-334.05	-79.84
0.2331	12751	-338.11	-80.81
0.2656	11190	-336.56	-80.44

Av. ΔHobs. = -337.06 ± 0.58 KJ mole^{-1}

= -80.56 ± 0.14 Kcal mole^{-1}

TABLE Adiabatic Calorimetric Results of Step(I) in Thermodynamic Cycle for Diphosphorus tetraiodide - boron tribromide (1:2) adduct referring to the following reaction in carbon disulphide (200 ml.) at 25°C.

$$P_2I_4 2BBr_3 \text{ (solid)} + CS_2 \text{ (liq.)} = (P_2I_4 2BBr_3)(CS_2)$$

Wt. $P_2I_4 2BBr_3$ (g)	$N(CS_2 : P_2I_4 2BBr_3)$	ΔHobs. KJ mole^{-1}	ΔHobs. Kcal mole^{-1}
1.0973	2564	-114.01	-27.25
1.0257	2743	-114.05	-27.26
1.0718	2625	-108.66	-25.97
1.0710	2626	-109.83	-26.24
1.0051	2799	-113.17	-27.05

Av. ΔHobs. = -111.92 ± 1.13 KJ mole^{-1}

= -26.75 ± 0.27 Kcal mole^{-1}

(1) All operations were performed under scrupulously dry conditions and under an inert atmosphere of nitrogen. Excess BBr_3 (1.3214 = 0.5 ml.) added to test these conditions.

(2) This was slow reaction. The fore-run was of 10 min., main reaction period 30 min., and aft-period readings were taken up to 130 min.

(3) Equal area method was used to locate the position of R_1 R_2 and R_3 R_4 on graph. A weighted (precalibrated) planimeter was used to measure the area.

TABLE Adiabatic Calorimetric Results of Step (2) in Thermodynamic cycle for Diphosphorus tetraiodide-boron tribromide (1:2) adduct referring to the following reaction in carbon disulphide (200 ml.) at 25°C. $N(CS_2:BBr_3) = 249$.

$$P_2I_4\ (\text{cryst.}) + (2BBr_3\ (\text{liq.}))\ (CS_2) = (P_2I_4 + 2BBr_3)\ (CS_2)$$

Wt. P_2I_4 (g)	$N(CS_2:P_2I_4)$	Δ Hobs. KJ mole^{-1}	Δ Hobs. Kcal mole^{-1}
0.5250	2850	117.69	-28.13
0.5372	2786	118.45	-28.31
0.5314	2816	118.45	-28.31
0.5382	2780	120.25	-28.74
0.5120	2923	117.99	-28.20

Av. Hobs. = -118.57 ± 0.46 KJ mole^{-1}

= -28.34 ± 0.11 Kcal mole^{-1}

(1) This was slow reaction. The fore-run was 10 min., main reaction 30 min. and after-run readings were recorded up to 140 min.

(2) All operations under an innert atmosphere of nitrogen.

(3) Boron tribromide added 2.6424g (= 1 ml.)

TABLE C.T.E. Calorimetric Results of Step (3) in Thermodynamic Cycle for Phosphorus tetraiodide - boron tribromide (1:2) adduct referring to the following reaction in carbon disulphide (200 ml.) at 25°C

$$BBr_3\ (liq.) + CS_2\ (liq.) = (BBr_3)\ (CS_2)$$

Wt. BBr_3 (g)	$N(CS_2:BBr_3)$	$\Delta H_{obs.}$ KJ $mole^{-1}$	$\Delta H_{obs.}$ Kcal $mole^{-1}$
1.4194	464	1.09	0.26
1.3080	504	1.09	0.26
1.3593	484	1.13	0.27
1.3111	502	1.09	0.26
0.8111	812	1.13	0.27
0.8048	819	1.13	0.27
1.0227	644	1.13	0.27
0.9951	662	1.13	0.27

Av. $\Delta H_{obs} = 1.13 \pm 0.004$ KJ $mole^{-1}$,
$= 0.27 \pm 0.001$ Kcal $mole^{-1}$

(1) All operations were performed under scrupulously dry conditions.

TABLE C.T.E. Calorimetric Results of Pentabromophosphorane - Boron Tribromide (1:1) adduct referring to the following reaction in water (150 ml.) at 25°C.

$$PBr_5BBr_3 \text{ (solid)} + 7H_2O \text{ (liq.)} = (H_3PO_4 + H_3BO_3 + 8HBr) \text{ (sol.)}$$

Wt. PBr_5BBr_3 (g)	$N(H_2O:PBr_5BBr_3)$	ΔHobs. KJ mole^{-1}	ΔHobs Kcal mole^{-1}
0.2136	26614	-745.46	-178.17
0.2150	26433	-751.11	-179.52
0.2300	24709	-746.97	-178.53
0.2240	25371	-749.19	-179.06
0.2261	25135	-752.95	-179.96
0.2160	26311	-749.35	-179.10

Av. ΔHobs. = -749.19 ± 1.09 KJ mole^{-1}

-179.06 ± 0.26 Kcal mole^{-1}

SECTION-III. RESULTS

CHAPTER SEVEN: THERMAL ANALYSIS RESULTS

Thermal Analysis Results

This chapter presents the results of the thermal analysis of phosphorus-phosphorus bonded compounds and certain molecular adducts. The aim of the study were: (i) Qualitative analysis to determine (a) melting points, (b) investigation of decompositional modes (especially in diphosphorus tetraiodide), (ii) quantitative analyses were performed to collect thermodynamic data (i.e. transition energy at fusion or phase change, as in pentaphenylcyclopentaphosphine and polymeric phenylphosphine). The heat of fusion of polymeric phenylphosphine; with respect to heat of fusion of polyethylene[43] , are used to determine the percentage crystallinity. All operations were performed under nitrogen atmosphere. The reproducibility of the results presented here was checked at least thrice in each compound.

The types of thermal analyzers used in this work were:

(i) Differential Scanning Calorimeter model 1B (DSC-1B) Perkin Elmer.

(ii) Thermogravimetric Analyser (TGA) Netzsch model 404 fully automatic.

(iii) Differential Thermal Analyzer (DTA) Du Pont with 900 thermal analyzer (Basic Unit) and Standard D.T.A. cell (Quartz Cover).

Thermal Analyzers and Programming

(i) The D.S.C. 1B (Perkin Elmer) instrument was operated under the following conditions throughout this work unless otherwise mentioned

Sample Holder	: volatile sample pan constructed from aluminium with cover
Reference Holder	: Empty pan with cover (as above)

Wt. of Sample and Holder : Ca. 15 mg.

Range : 2 millicalorie per sec. (m. cal. sec^{-1}) full scale difflection (F.S.D.)

Scan : 8°C per minute

Chart : 60 inch per hour

Gas flow : 20 ml. per minute, nitrogen

Heater : Platinum wire

Temperature detector : Platinum resistance thermometer

Balance : "Cahn Gram" Electrobalance with accuracy 10^{-6}g.

(ii) D.T.A. Du Pont analyzer was operated under the following conditions throughout this work unless otherwise stated.

Sample Holder : Aluminium pan (6.6 m.m. internal diameter) with cover weighing 3 mg.

Reference Holder : Aluminium pan with lid containing alumina

Sample size : Ca. 0.5 to 100 mg.

Sample thermocouple : Chromel-Alumel

Differential thermocouple: Chromel-constantan

Control thermocouple : Chromel-Alumel

Calorimetric sensitivity : 0.2 milli cal sec^{-1} in^{-1} (based on 40 milli volt recorder at ambient)

Calorimetric precision : ca. ± 1.0 %

Temperature repeatability : ± 1°C

Heater : 200 Watt. Nichrome Wound

Atmosphere : Nitrogen

(iii) Thermogravimetric Analyser (T.G.A.) fully automatic Netzsch model 404.

Sample Holder	: Specially designed hexagonal and round cells(and cover constructed from) stainless steel in this laboratory weighing 4.890g. and 0.1 mm. hole in the cover
Holder capacity (maximum)	: Ca. 2g.
Gas flow	: 125 c.c. min^{-1} nitrogen
Chart Speed	: 12 cm. hr^{-1}
Heating rate	: $1^{\circ}\text{C min}^{-1}$

Table Differential Scanning Calorimetry Results for Indium Standard

Mode of run:

Weight of Indium = 0.8465 mg.

Temperature range = 40 - 190°C

Analysis of Thermogram:

Transition temperature : 156.5°C (lit.[48] 156.5°C)

Transition range : 155-157°C

Type of Peak : Endothermic, sharp (Height, 18.2 cm.)

Area under Peak : 0.043 planimeter unit (P.U.) cal. mole^{-1}

$\Delta H_{(\text{fusion})}$: 779.6 cal. mole^{-1} (lit.[48] 780 cal. mole^{-1})

Specific heat : 0.05 cal. $g.^{-1}\ {}^{o}C^{-1}$ (lit.[211] 0.05)

(1) Indium standard is used as calibrant for accurate measurements of temperature and heat content. (see graph on P.147)

(2) The calculations for heat of transition of an unknown sample with reference to Indium (In) are performed as follows:

Peak area (In) = Wt. (In) x Specific heat (In)

Peak area (Sample) = Wt. (Sample) x Specific heat (Sample)

Therefore the heat of transition is given by

$$\Delta H_{(\text{Sample})} = \Delta H_{(\text{In})} \times \frac{\text{Wt. (In)}}{\text{Wt. (Sample)}} \times \frac{\text{Peak area (Sample)}}{\text{Peak area (In)}}$$

Where Wt. is in mg., and $\Delta H_{\text{In (fusion)}}$ = 6.79 milli cal. mg.^{-1} (or 6.79 cal. g^{-1})

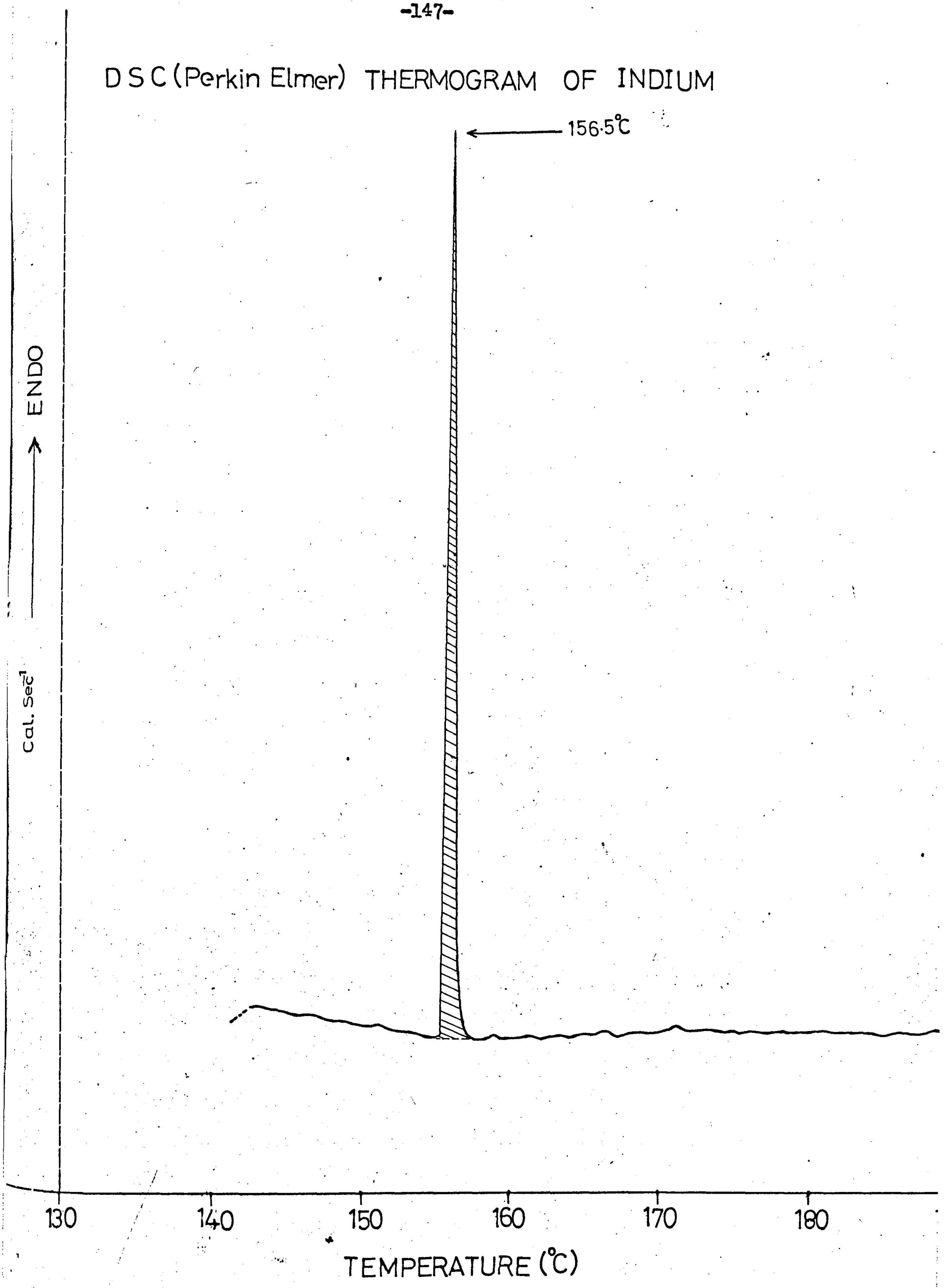

DSC (Perkin Elmer) THERMOGRAM OF INDIUM

Fig. Thermograph for the fusion of Indium: Fusion temperature, 156.5 $^{\circ}$c and ΔHfus. = 779.6 cal. mole^{-1}.

Table Differential Scanning Calorimetry Results for Pentaphenylcyclopentaphosphine

1st mode of run:

Weight of $(C_6H_5P)_5$: 1.242 mg.

Temperature range : 40 - 350°C (Heating)

Analysis of Thermogram:

1st Transition temperature : 86°C (Cf. the transition in piperidine)[85]

Transition range : 85 - 105°C

Type of peak : Exothermic, sharp, (Height, 6 cm.)

Area under peak : 0.1190 P.U.

Transition energy : 12.77 cal. g^{-1} (6.89 kcal per $(C_6H_5P)_5$)

2nd Transition temperature : 154°C (lit.[85] m.p. 149-156°C)

Transition range : 138 - 157°C

Type of peak : Endothermic, melting, sharp, (Height, 7 cm.)

Area under peak : 0.1207 P.U.

Transition energy (ΔH_{fusion}) : 12.95 cal. g^{-1} (=6.99 kcal per $(C_6H_5P)_5$)

2nd mode of run : 350 - 50°C (cooling) and

3rd mode of run : 40 - 350°C (heating)

(1) Actual graph showing transition peak and the area measured by planimeter is shown on P. 149 .

(2) Additional run on the same sample weighing 5 mg. and range 4 m. cal. sec^{-1} produced no significant change on the part of the thermogram.

(3) The Exothermic transition peak at 86°C (Cf. with D.T.A. same temperature transition, see graph on P. 151) is indicative of a probable phase change[85] occuring in solution (i.e. piperidine) at about the same temperature (Ca. 80°C). It is possible that these two facts are connected. In this work three attempts were made with little success to convert $(C_6H_5P)_5$ to $(C_6H_5P)_n$. Hence a direct synthetic route was investigated (see P. 48 under synthesis).

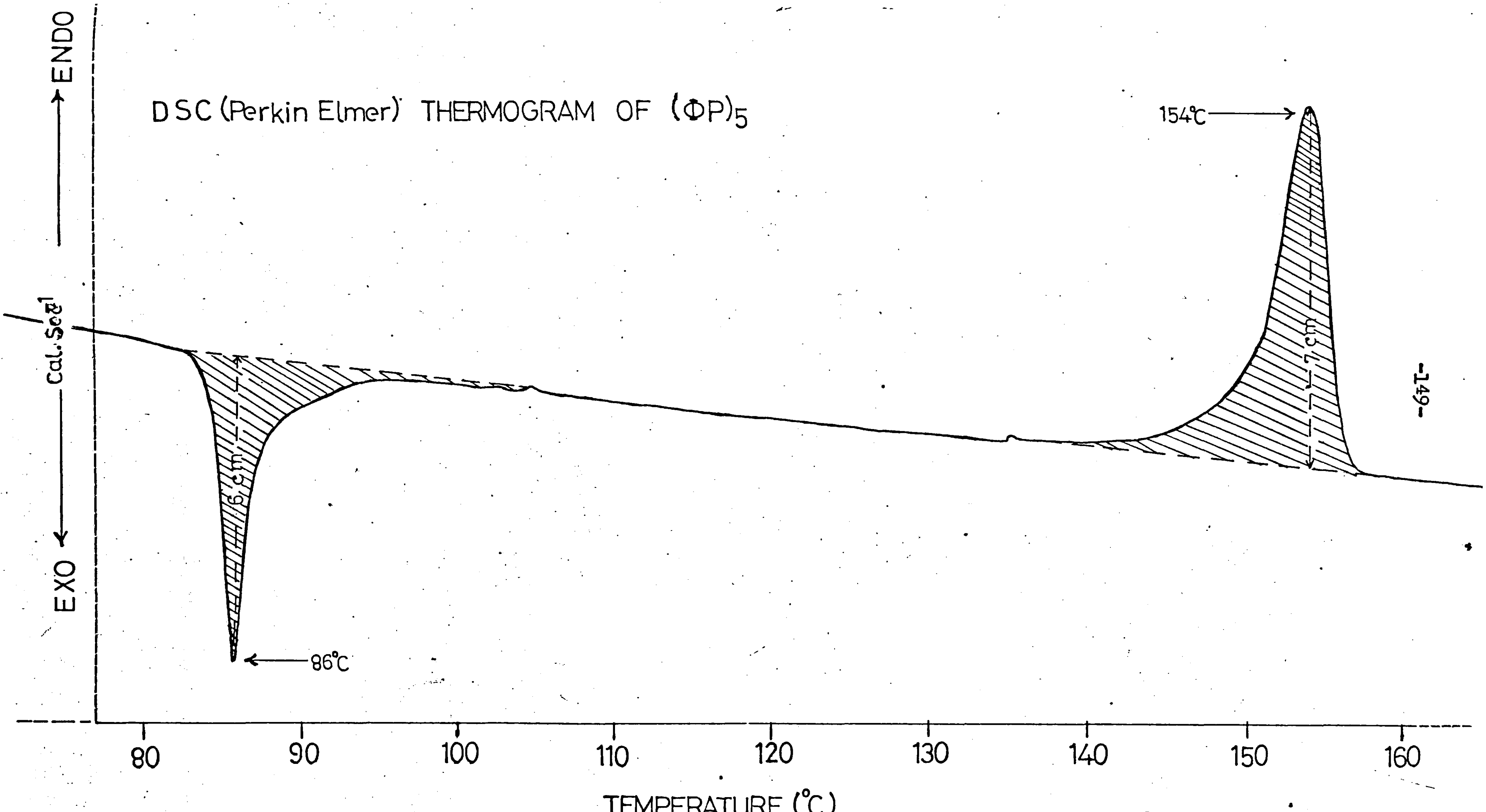


Fig. Thermograph for pentaphenylcyclopentaphosphine (form A) showing exothermic peak at 86°C and melting and endothermic peak at 154°C

Table Differential Thermal Analysis Results for Pentaphenylcyclopentaphosphine

Mode of run:

Weight of $(C_6H_5P)_5$: 7 mg.
Temperature range : 30 - 200°C
Rate of heating : 10°C min^{-1}
ΔT : 0.5°C $inch^{-1}$
Temperature scale : 20°C $inch^{-1}$

Analysis of Thermogram

1st Transition temperature : 86°C (Cf. the transition in piperidine)[85]
Transition range : 70 - 90°C
Type of peak : Exothermic, sharp flattening (Height, 5.7 cm.)

2nd Transition temperature : 154°C
Transition temperature : 152 - 162°C
Type of peak : Endothermic, melting, sharp (Height 7.3 cm.)

(1) Characteristic melting peak of monoclinic type of crystal was identified for pentaphenyocyclopentaphosphine (Also private communication with Dr. I. C. Wylie Du Pont Company (U.K.) Ltd., their Ref. ICW:SO dated 1st August, 1968.)

(2) Exothermic peak at 86°C before melting point of $(C_6H_5P)_5$ shows that most probably phase change is taking place.

(3) Exothermic peak at 86°C is also evident on the D.Sc. thermogram. (See graph on P. 151).

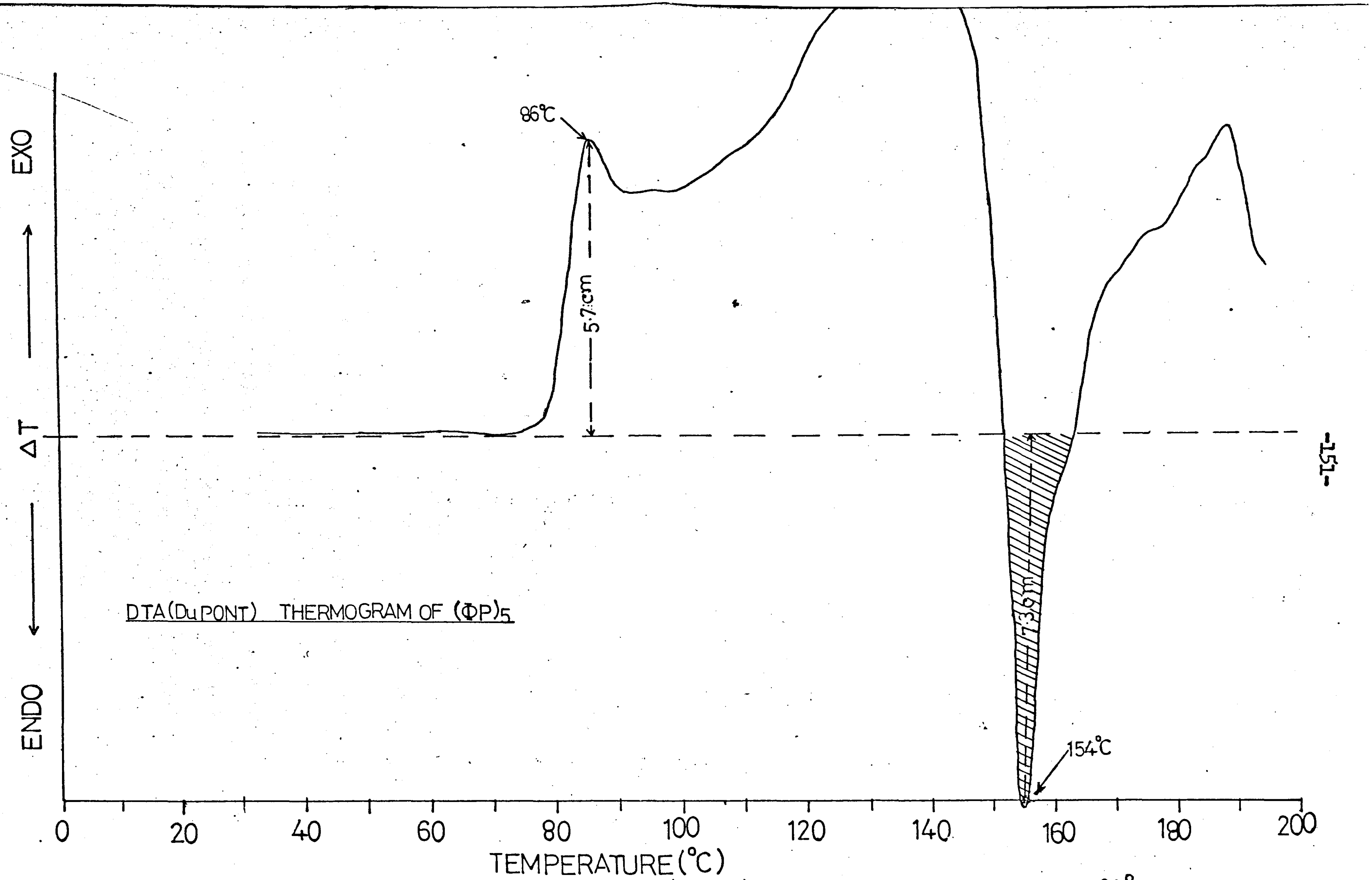


Fig. Thermograph of pentaphenylcyclopentaphosphine (form A) showing exothermic peak at Ca. 86 °C and the melting endotherm at 154 °C.

Table Differential scanning calorimetry Results for Hexaphenylcyclohexaphosphine*

1st Mode of run:

Weight of $(C_6H_5P)_6$: 0.915 mg. (single crystal)

Range : 4 m cal. sec^{-1}

Temperature range : 40 - 210°C

Analysis of Thermogram

1st Transition temperature : 76°C

Transition range : 70 - 80°C

Type of peak : Endothermic, broad softening type, (Height 0.5 cm)

2nd Transition temperature : 130°C

Transition range : 110 - 131°C

Type of peak : Twin exothermic, broad followed by sharp. (Height: broad 1.5 cm., sharp, 2 cm.)

3rd Transition temperature : 190°C (lit.[85] 190°)

Transition range : 172 - 195

Type of peak : Enothermic melting, broad softening peak (Height, 1 cm.)

(1) Transition at 76°C shows softening effect of crystal followed by, probably, a phase change at 130°C, and finally melts at 190°.

(2) Lit. also refers to (i) 130-155°C for the clathrate compound of composition one molecule of benzene to six C_6H_5P groups (ii) thermal change produces $(C_6H_5P)_5$ from $(C_6H_5P)_6$ (iii) solvents like C_6H_5H and HCl also bring about the conversion of $(C_6H_5P)_6$ to $(C_6H_5P)_5$.

*This sample was donated by Dr. L. Maier

2nd Mode of run:

Weight of $(C_6H_5P)_6$: 3.130 mg. (four crystals)
Temperature range : 40 - 300°C (heating)

Analysis of Thermogram

1st transition temperature : 76°C
Transition range : 70 - 80°C
Type of peak : Endothermic, broad softening type to sharp (Height, 2 cm.)

2nd transition temperature : 130°C
Transition range : 110 - 132°C
Type of peak : Twin exothermic, broad followed by sharp. (Height: broad 4.5 cm., sharp 5 cm.)

3rd transition temperature : 190°C
Transition range : 160 - 205°C
Type of peak : Endothermic melting, broad softening peak. (Height, 1 cm.)

(1) Exothermic transition at 130°C suggests possible phase change. The literature refers to a phase change with no definite temperature and phase change occuring in solution phase (i.e. C_6H_6 and HCl). It is possible that these facts are connected.

Table Differential Scanning Calorimetry Results for polymeric phenylphosphine referring to transition energy and percentage crystallinity

1st Mode of run:

Weight of $(C_6H_5P)_n$: 2.085 mg.
Temperature range : 40 - 350°C (Heating)

Analysis of Thermogram

1st transition temperature : 86°C
Transition range : 75 - 105°C
Type of peak : Twin exothermic, sharp followed by broad (Height: sharp 3.3 cm., broad 1 cm.)
Area under peak : 0.1127 P.U.
Transition energy : 7.22 cal. gm.$^{-1}$ (0.78 kcal mole^{-1} (C_6H_5P)

2nd transition temperature : 285°C (lit.^{61} 252 - 305)
Transition range : 190 - 325°C
Type of peak : Endothermic melting, broad (Height, 3 cm.)
Transition energy : 41.56 cal. g^{-1} (4.49 kcal mole^{-1} (C_6H_5P))

2nd Mode of run: : 350 - 50°C (Cooling)
3rd Mode of run: : 40 - 350°C (Reheating)

(1) No significant peak appeared in 2nd and 3rd runs. Also two other such type of thermograms were run on different quantities of the same sample. Thermograms of similar types were produced.

(2) Exothermic transition peak at 86°C is indicative of phase change. Literature[85] refers to phase change $(C_6H_5P)_n$ to $(C_6H_5P)_5$ at no definite temperature and also occuring in solution phase (i.e. diphenyl ether). It is possible these facts are connected.

(3) 2nd and 3rd mode of runs suggest that direct heat treatment to crystalline polymeric phenylphosphine produces partial phase change.

(4) The percentage crystallinity of polymeric phenylphosphine is measured in this work via heat of fusion and is expressed as

$$\% \text{ crystallinity } (C_6H_5P)_n = \frac{\Delta H\text{fusion } (C_6H_5P)_n}{\Delta H_{\text{fusion}} \text{ Polyethylene}} \times 100$$

where

$\Delta H_{\text{fusion}} (C_6H_5P)_n = 41.56 \text{ cal. } g^{-1}$

$\Delta H_{\text{fusion}} \text{ Polyethylene} = 68.4 \text{ cal. } g^{-1}$

$$\% \text{ crystallinity } (C_6H_5P)_n = \frac{41.56}{68.6} \times 100 = \underline{74.5}$$

(5) The presence of 74.5% crystallinity suggests heterogneity and the substance does not possess sharp melting point (literature[61] give m.pt. 252-285°C)

Table Thermogravimetric Analysis Results for Diphosphorus tetraiodide referring to decompositions

Mode of run:

Weight of P_2I_4 : 184.2 mg.

Temperature range : 20 - 285°C

Range (Full scale deflection) : 200 mg.

Heating rate 1°C min^{-1}

Chart speed 2 mm. min^{-1}

Detailed Analysis of Thermogram

ΔW = weight change (mg.)

Δt = time in minutes

NORMAL THERMOGRAM		DERIVATIVE OF THERMOGRAM		
Weight Loss (mg)	Temperature (°C)	ΔW	Δt	$\Delta W/\Delta t$ ($x\ 10^{-2}$)
0.00	20	0.0	45	0
0.00	65			
0.80	70	0.80	5	17
1.20	75	0.40	5	8
1.60	80	0.40	5	8
2.40	85	0.80	5	16
3.20	90	0.80	5	16
3.20	95	0.00	5	0
4.00	100	0.80	5	16
4.40	105	0.40	5	8
4.80	110	0.40	5	8

5.20	115	0.40	5	8
5.60	120	0.40	5	8
6.00	125	0.40	5	8
6.08	130	0.08	5	2
6.88	135	0.80	5	16
7.12	140	0.24	5	5
7.20	145	0.08	5	2
7.20	150	0.00	5	0
7.28	155	0.08	5	2
7.60	160	0.32	5	6
7.76	165	0.16	5	3
8.00	170	0.24	5	5
8.40	175	0.40	5	8
9.60	180	1.20	5	24
10.40	185	0.80	5	16
11.20	190	0.80	5	16
12.00	195	0.80	5	16
13.20	200	1.20	5	24
14.40	205	1.20	5	24
16.40	208	2.00	3	66
17.60	210	1.20	2	60
18.40	213	0.80	0	40
22.40	215	4.00	5	80
24.80	220	2.40	5	48
28.56	225	3.76	5	75
32.80	230	4.24	5	85
37.60	235	4.80	5	96

42.40	240	4.80	5	96
48.40	245	6.00	5	120
55.40	250	7.00	5	140
64.40	255	9.00	5	180
74.40	260	10.00	5	200
86.40	265	12.00	5	240
100.00	270	14.00	5	280
116.00	275	16.00	5	320
134.40	280	18.40	5	368
154.40	285	20.40	5	408
170.40	290	16.00	5	320

(1) Another run on the same sample, weighing 430.1 mg., with a heating rate of 5°C $\min^{-1}$ and with nitrogen flow 150 cc. $\min^{-1}$ was performed. A similar type of thermogram was obtained (as above), with no sign of decomposition before melting.

(2) That, there is negligible weight loss before melting point, hence the possibility of decomposition prior to m.pt. is very remote.

(3) A derivative graph plot of $\Delta W / \Delta t$ vs. temperature showed no sign of decomposition before melting.

TABLE - Differential Thermal Analysis Results for Diphosphorus tetraiodide-Boron tribromide (1:2) Adduct

Mode of Run:

Weight of $P_2I_4 2BBr_3$: 15 mg

Temperature range : 23-300°C

Temperature scale : 20°C $inch^{-1}$

Rate of heating : 10°C min^{-1}

ΔT : 0.5°C $inch^{-1}$

Analysis of Thermogram

1st transition temperature : 100°C

Transition range : 82-110°C

Type of peak : Endothermic, broad sharp (Height 1.7 cm.)

Peak area : 0.50 sq. in.

2nd transition temperature : 122°C

Transition range : 110-131°C

Type of peak : Endothermic, broad sharp (Height 2 cm.)

Peak area : 0.66 sq. in.

(1) The transition peaks area was measured by extrapolation, by cutting and weighing and also by using a weighted planimeter.

(2) It is possible that the first endotherm corresponds to the loss of two molecules of boron tribromide (cf. normal b.pt. BBr_3 = 91°C).

(3) It is equally likely that the second endotherm corresponds to the melting of diphosphorus tetraiodide (cf. m.pt. P_2I_4 = 124.5°C).

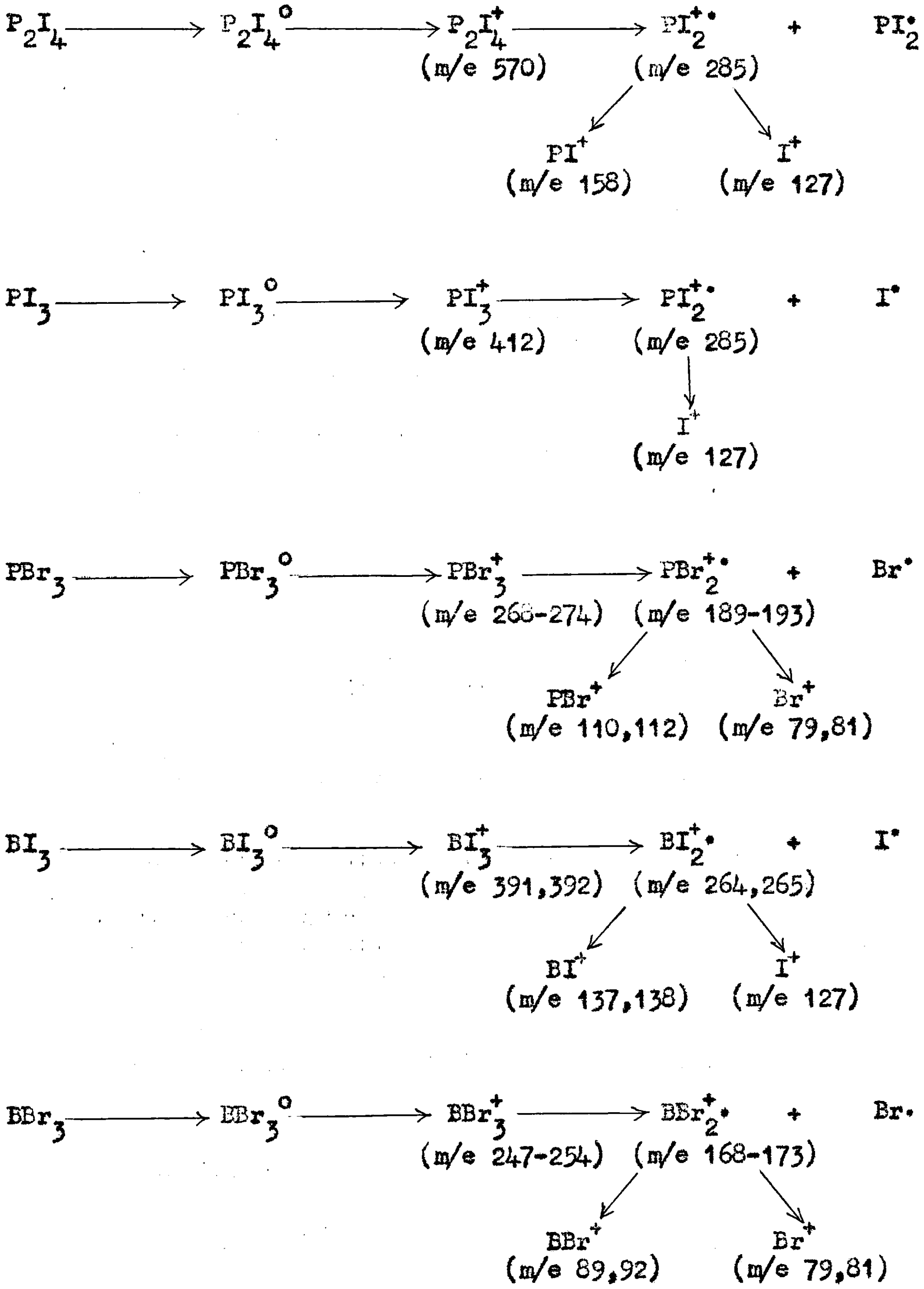
(4) TGA runs on a model 404 Netzsch indicates no appreciable weight loss until 138°C. Thereafter regular weight loss occurred (ca. 0.7 mg. deg^{-1}) until an inflexion at ca. 250°C.

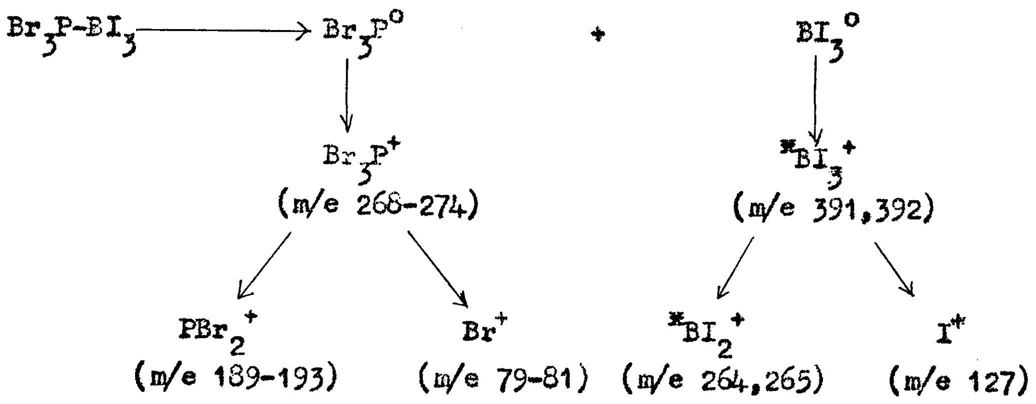
Similar studies on Du Pont T.G.A. 950 equipment indicated steady weight loss from 20 to 100°C (ca. 20%) followed by a more rapid loss to 200°C (a further 50%) followed by a 5% loss over another 350°C. No suitable conclusion as to the mode of decomposition can be derived from these results.

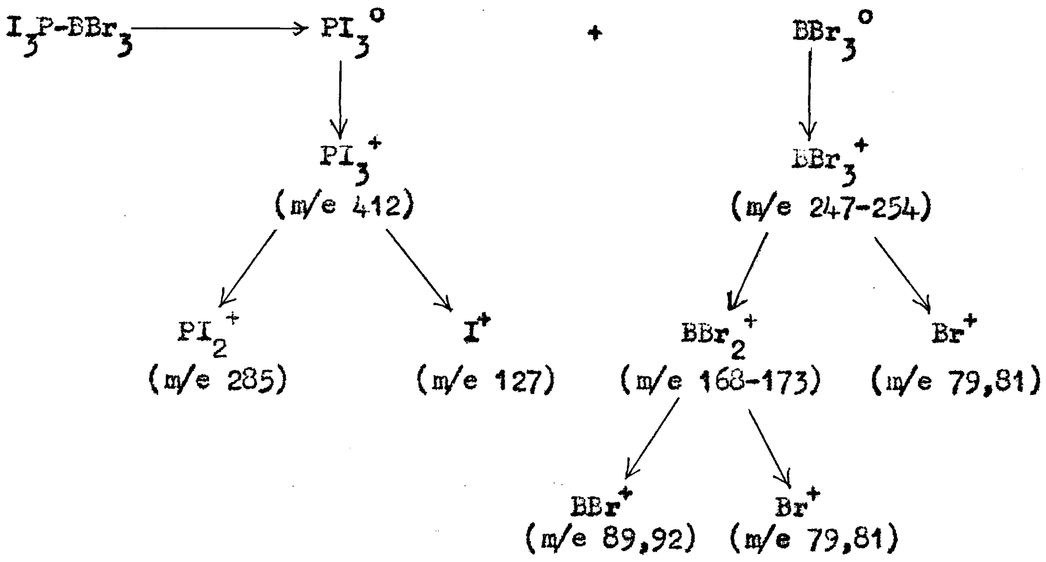
SECTION-III. RESULTS

CHAPTER EIGHT: MASS SPECTROMETRIC RESULTS

Probable mode of cracking obtained by electron impacts for the compound containing phosphorus-phosphorus bond, Phosphorus (III), Boron (II and molecular adducts of phosphorus (III).







o = shows neutral molecule in gaseous state

* = unobserved species

\- = a range of m/e data due to isotope splitting

• = unpaired electron

Table Mass Spectrum of Diphosphorus tetraiodide and the analysis of major significant peaks (M.S.P.)

Spectrometer : AEI model MS902 (double focusing)
Insertion mode : Direct inlet system
Source temperature : 285°C

Electron Energy (input) : 70 ev

m/e	31	62	63-64	124	127
%	17.0	35.7	8.5	51.0	100
m/e	128	158	254	285	570
%	40.8	44.2	51.0	68.0	85.0

M.S.P. (m/e)	Probable Species	Remarks
31	P^+	
62	P_2^+	
63 - 64	I^{++}/HI^{++}	
124	P_4^+	Possibly arising from elemental phosphorus in sample.
127	I^+	Base peak, 60 mm, 100%
128	HI^+	
158	PI^+	
254	I_2^+	Possibly from elemental iodine
285	PI_2^+	
443	$P_2I_3^+$	
570	$P_2I_4^+$	

(1) Peak heights less than 2% are not accounted for.

(2) Mass Spectrometry at School of Pharmacy their Ref. No: 68/327 (iv) dated 14.3.68.

(3) Under similar conditions except source temperature 190°C, probe at 150°C three more spectra were run on the same sample at ERDE, Waltham Abbey, using AEI model MS2H mass spectrometer, their Rf. No: 166. No significant change in the location of peaks or percentage abundance was noticed. The appearance potential (A.P.) by the method of Lossing[194] et al for one of the runs for the following process gave the value of $(PI_2^+)_{P_2I_4} = 12.8$ ev ± 0.15 ev.

$$P_2I_4 + e \longrightarrow PI_2^+ + PI_2 + 2e. \qquad AP.(PI_2^+)_{P_2I_4}$$

Table Mass Spectrum of Triiodophosphine and the analysis of major significant peaks

Spectrometer : AEI model MS 902 (double focusing)

Insertion mode : Direct inlet system

Source temperature : 155°C

Electron energy (input) : 70 ev

m/e	126	127	128	165	195
%	40.0	100.0	42.0	36.0	20.0
m/e	285	412			
%	72.2	84.6			

M.S.P. (m/e)	Probable Species	Remarks
127	I^+	Base peak, 25 mm., 100%
285	PI_2^+	
412	PI_3^+	

(1) Peak heights less than 2% are not accounted for.

(2) Mass spectrometry at School of Pharmacy their Ref. No: 68/533 dated 6.5.68.

(3) Under similar conditions another three spectra were run on the same sample, at ERDE, Waltham Abbey, using AEI model MS2H mass spectrometer. No significant change in the location of peaks or percentage abundance was noticed. The appearance potential measurements (A.P.) by the method of Lossing[194] et al, for one of the runs for the following process gave the value of

$(PI_2^+)_{PI_3} = 11.9$ ev ± 0.15

$PI_3 + e \longrightarrow PI_2^+ + I + 2e.$ A.P. $(PI_2^+)_{PI_3}$

Table Mass Spectrum of Tribromophosphine and the analysis of the major significant peaks

Spectrometer : AEI MS 902 (double focusing)

Insertion mode : Direct

Source temperature : 250°C (Probe at 30°C)

Electron energy (input) = 70 ev.

m/e	79	80	81	82	110
%	90	100	80	80	23.0
m/e	111	189	191	270	271
%	22.0	40.0	80.5	26.2	25.0

M.S.P. (m/e)	Probable Species	Remarks
79	Br^+	Base peak (10 mm, 100%)
80		
81	HBr^+	
82		
110	PBr^+	
111		
189	PBr_2^+	
191		
270	PBr_3^+	
271		

(1) Peak heights less than 2% are not accounted for.

(2) Mass spectrometry performed at School of Pharmacy their Ref. No: 70/849 dated 23.7.69.

Table Mass Spectrum of Boron Triiodide and the analysis of the major significant peaks

Spectrometer : AEI MS 902 (double focusing)
Insertion mode : Direct
Source Temperature : 150°C

Electron energy (input) = 70 ev.

m/e	28	36	43	49	62
%	9.2	2.1	2.5	2.5	9.6
m/e	64	127	128	137	138
%	8.3	95.9	71.3	4.2	16.9
m/e	142	173	254	264	265
%	7.5	4.2	37.5	25.0	100.0
m/e	300	391	392	396	414
%	2.5	16.6	70.8	2.0	20.8
m/e	426	464	502		
%	12.5	16.6	29.2		

M.S.P. (m/e)	Probable Species	Remarks
127	I^+	
137 138	BI^+ (BI)	
264 265	BI_2^+	Base peak, 24 mm, 100%
391 392	BI_3^+	

(1) Peak heights less than 2% are not accounted for.

(2) Mass spectrometry at School of Pharmacy
their Ref. No: D 1370/0 dated 15.4.70.
Ref. No: 69/1231 dated 9.10.69.

(3) Exact mass number at 364 and 392 were determined by introducing perfluorobutylamine (mol. wt. 671) as reference innert compound. (Ref. No: D 1370/0 dated 15.4.70.)

Table Mass Spectrum of Boron tribromide[212] and the analysis of the major significant peaks

Spectrometer : AEI MS 902 (double focusing)
Insertion mode : Cold
Source Temperature : 250°C

Electron energy (input) = 70 ev

m/e	18	28	35	36	38
%	2.2	2.2	3.9	4.0	13.9
m/e	40	41	44	79	80
%	2.6	2.6	2.6	39.0	100.0
m/e	81	82	125	127	168
%	33.3	94.4	7.2	10.1	12.9
m/e	170	171	173	250	252
%	4.4	25.0	12.2	6.9	6.9

M.S.P. (m/e)	Probable Species	Remarks
79	Br^+	Base peak (18 mm, 100%)
80		
82	HBr^+	
168	BBr_2^+	
173		
250	BBr_3^+	
252		

(1) Peak heights less than 2% are not accounted for.

(2) Mass Spectrometry performed at School of Pharmacy their Ref. No: 70/450 dated 10.4.70.

Table   Mass spectrum of tribromophosphine-boron triiodide (1:1) adduct

Spectrometer : AEI MS 902 (double focusing)

Insertion mode : Direct

Source Temperature : 260°C

Electron energy (input) = 70 ev

m/e	31	34	35	36	37
%	4.0	9.0	27.0	4.0	12.5
m/e	38	39	41	43	44
%	4.0	2.5	5.3	5.0	2.5
m/e	55	57	62	62-63	64
%	2.5	3.0	8.0	3.4	2.7
m/e	65	69	79	80	81
%	3.4	2.3	42.0	100.0	46.0
m/e	82	91	110	112	124
%	96.1	11.5	3.8	3.8	11.5
m/e	127	128	142	145	147
%	42.3	54.0	13.0	3.8	4.0
m/e	156	158	188-189	190	192
%	3.8	5.7	7.9	7.9	15.4
m/e	236	238	254	270	272
%	8.4	7.9	3.9	4.6	5.0
m/e	284	315	317	319	364
%	5.0	3.0	6.5	3.9	5.3
m/e	365	407			
%	5.3	5.3			

(1) Base peak at m/e 80 (26 mm, 100%)

(2) Peak heights less than 2% are not accounted for.

(3) Mass spectrometry at School of Pharmacy their Ref. No: 69/693 dated 14.5.69.

(4) No significant peak observed between 407-663 (mol. wt. of compound)

Table Mass Spectrum analysis of tribromophosphine-boron triiodide (1:1) adduct referring to major significant peaks

Major peaks m/e	Probable Species	Remarks
31	P^+	
62	P_2^+	
79		
80	Br^+	Base peak (26 mm, 100%)
81		
82	HBr^+	HBr probably formed due to reaction with wall of mass spectrometer
124	P_4^+	Possibly arising from elemental phosphorus in sample as phosphorus in vapour phase is tetrahedral P_4 molecules.
127	I^+	
128	HI^+	
142	P_2Br^+	
158	PI^+	
188-189	P_2I^+	
190	Br_2P^+	
192		
238	$PBrI^+$	
254	I_2^+	
270		
272	P^+Br_3	
284	PI_2^+	
317		
319	Br_2PI^+	
364		
365	PI_2Br^+	

Table Mass Spectrum of triiodophosphine-boron tribromide (1:1) adduct

Spectrometer : AEI MS 902 (double focusing)

Insertion mode : Direct

Source Temperature : 260°C

Electron energy (input) = 64 ev

m/e	11	15	28	32	35
%	6.0	3.6	15.1	3.0	3.0
m/e	61	76	79	80	81
%	3.0	5.1	21.2	30.3	21.2
m/e	82	89	90	91	92
%	30.3	2.7	10.3	2.4	10.3
m/e	124	125	127	128	142
%	9.1	3.6	18.2	15.1	3.3
m/e	158	167	168	169	170
%	5.1	15.1	51.5	27.3	100.0
m/e	171	172	188	190	192
%	14.8	48.5	3.0	5.4	2.7
m/e	236	238	246	247	248
%	6.1	6.1	3.0	11.2	8.8
m/e	249	250	251	252	253
%	30.3	7.9	27.3	2.7	24.2
m/e	285	317-318	364	365-366	412
%	6.1	2.4	4.5	4.2	7.6

(1) Base peak at m/e 170 (33 mm, 100%)

(2) Peak heights less than 2% are not accounted for.

(3) Mass spectrometry at School of Pharmacy (University of London) Intercollegiate Research Service their Ref. No: 69/644 dated 7.5.69.

(4) No significant peak observed between 413-663 (mol. wt. of compound).

Table Mass Spectrum analysis of triiodophosphine-boron tribromide (1:1) adduct referring to major significant peaks

M.S.P. (m/e)	Probable Species	Remarks
79 80 81 82	Br^+/HBr	HBr probably formed by reaction with the wall of the spectrometer
89 90 91 92	BBr^+(BBr)	
124	P_4^+	Possibly arising from elemental phosphorus in sample.
127 128	I^+ HI^+	
168 169 170 171 172	BBr_2^+	Base peak at m/e 170, 33 mm, 100%
247 248 249 250 251 253	BBr_3^+	
285	PI_2^+	
412	PI_3^+	

SECTION-III. RESULTS

CHAPTER NINE: EFFUSION MANOMETRIC RESULTS

Effusion Manometric Results

This chapter presents the results for the latent heat of sublimation determined via experimental measurements of vapour pressure as a function of temperature of:

(i) Ferrocene (as test compound)

(ii) Triiodophosphine

(iii) Diphosphorus tetraiodide

These data were obtained from an effusion manometer constructed in this laboratory. The basic equations for deriving vapour pressure data are as follows:

$$p = \frac{W}{tA}\sqrt{\frac{2\pi RT}{M}} \times \frac{1}{K_c} \times \frac{1}{\delta_o} \quad \text{--------------------} (1)$$

$$p = \frac{W}{tA}\sqrt{\frac{2\pi RT}{M}} \times K_n \times \frac{1}{\delta_o} \quad \text{--------------------} (2)$$

$$p = \frac{W}{tA}\sqrt{\frac{2\pi RT}{M}} \times \left(\frac{3L + 8r}{8r}\right)\left(\frac{1}{1 + K_2 + r/2\lambda}\right) \times \frac{1}{\delta_o} \quad \text{--} (3)$$

where p = pressure (mm. Hg.)

W = weight loss (g.)

t = time (sec.)

A = area of the orifice ($cm.^2$)

R = gas constant, 8.3143×10^7 erg, deg^{-1}, $mole^{-1}$

T = absolute temperature ($t(c^o) + 273.15$) ^oK

M = molecular weight Ferrocene = 186.041

PI_3 = 411.6870

P_2I_4 = 569.5652

δ_o = 1

$\frac{1}{K_e}$ = 1.07158

K_n = 1.05415

r = 1.849×10^{-2} cm.

$$\lambda = \frac{kT}{\sqrt{2}\,\pi\,\sigma^2\,p} \qquad \left(= \frac{1}{\sqrt{2}\,\pi\,Nd^2} \right)$$

where

λ = mean free path (cm.)

k = Boltzmann's Constant, 1.3805×10^{-16} erg. $^{\circ}K^{-1}$

σ or d = effective collision diameter ($^{\circ}A$)

N = number density (or number of molecules per unit volume)

(for further details see ch. 5 p. 99)

The vapour pressure data derived from equation (1) and (2) are presented in this chapter as average values. While the data obtained from equation (3) are given as such. The relevant graphs are presented with and without the Hiby and Pahl correction factors to illustrate their magnitude. The corrected vapour pressure data are used to determine the latent heat of sublimation via the Clausius Clapeyron equation,

$$\log_{10} p = \frac{-\Delta H\ \text{sub.}}{2.3026\ RT} + C$$

where C = constant

The uncertainty interval for the slope of the $\log_{10}$ p vs 1/T plot was determined from the following expression

$$\pm \left[\sum_i r_i^2 / (n-2) \left(\sum_i x_i^2 - n\bar{x}^2 \right) \right]^{\frac{1}{2}}$$

where r = residual

n = no. of sets

$x = T^{-1}$

TABLE Comparison of the available literature data for the vapour pressure (P 298) and latent heat of sublimation (ΔH (c→g)) for ferrocene

LITERATURE	ΔH (c→g) 298		P 298 (mm.Hg)
	Kcal mole^{-1}	KJ mole^{-1}	
Edwards & Kington[196] (1962)	17.53 ± 0.10	73.34 ± 0.42	0.00684
Andrews & Westrum[200] (1969)	17.38 ± 0.13	72.72 ± 0.54	0.00714
This work	17.84 ± 0.96	74.64 ± 4.02	0.00680

Table Synopsis of Effusion Manometric Data

DATUM	VALUE
Weight of empty stainless steel cell (complete)	25.8161 g.*
Weight of Ferrocene (2/3 cell capacity)	1.7719 g.
Weight of PI_3 (2/3 cell capacity)	5.9657 g.
Weight of P_2I_4 (2/3 cell capacity)	6.1244 g.
Area of the orifice (A)	1,0740 x 10^{-3} $cm.^2$
Thickness of the gold foil (l)	2.6702 x 10^{-3} cm.
Radius of the orifice (r)	1.849 x 10^{-2} cm.
Radius of the foil (R)	8.729 x 10^{-1} cm.
Ratio of thickness to radius	1.444 x 10^{-1} cm.
Mean free path $\lambda_{Ferrocene}$ ca. $25^{o}C$	1.835 x 10^{-1} cm.
Mean free path λ_{PI_3} ca. $25^{o}C$	2.447 x 10^{-1} cm.
Mean free path $\lambda_{P_2I_4}$ ca. $55^{o}C$	4.809 x 10^{-1} cm.
Effective collision diameter including Vander Waals Radii d (or σ)	
$d_{Ferrocene}$	$7.36^{o}A$
d_{PI_3}	$8.56^{o}A$
$d_{P_2I_4}$	$9.85^{o}A$
ΔH (Ferrocene, $C \rightarrow g)_{298}$	74.64 ± 4.02 KJ $mole^{-1}$ (17.84 ± 0.96 Kcal $mole^{-1}$)
ΔH (PI_3, $C \rightarrow g)_{298}$	63.64 ± 3.60 KJ $mole^{-1}$ (15.21 ± 0.86 Kcal $mole^{-1}$)
ΔH (P_2I_4, $C \rightarrow g)_{298}$	69.87 ± 2.09 KJ $mole^{-1}$ (16.70 ± 0.50 Kcal $mole^{-1}$)

(1) Ferrocene : m. pt. 175 - 176°C (purified by a modification of the procedure of Edwards et. al[167]) was used in powdered form.

(2) Triiodophosphine : m. pt. 61°C, the samples of Dr. I. H. Wood of this laboratory and K. & K. laboratory Inc., California, (batch No: 17819) were used in powdered form.

(3) Diphosphorus tetraiodide : m. pt. 124.5°C prepared according to the method of German and Traxler[91] (see, synthesis on p. 49) and also a Koch-Light sample were used in powdered form.

(*Weight of cell after each experiment was checked and remained the same.)

TABLE Photomicrographic measurements on gold foil (linear magnification x 100) from effusion manometric cell

(i) Radius of Orifice (r)

(a) By Travelling Microscope : 1.8480×10^{-2} cm.

(b) By Weighted Planimeter : 1.8498×10^{-2} cm.

Radius of Orifice (r) : 1.849×10^{-2} cm.

(ii) Thickness of foil (l)* : 2.670×10^{-3} cm.

(iii) Radius of foil (R) : 8.729×10^{-1} cm.

$$* \; l = \frac{m}{\rho(R^2 - r^2)} \times \frac{1}{\pi}$$

Where

m = mass of foil = 0.1233g.

ρ = density of foil (AU) = 19.3g. ml^{-1}

TABLE Mercury Thermometer (N.P.L.B.S. 791, nitrogen filled) calibration against 2801A Quartz thermometer* (Hewlett Packard)

S (°C)	tu uncorrected (°C)	E.S.H. (°C)	E.S.C. (°C)	t corrected (°C)	Q corrected (°C)	± Δn (Q-t)
20.09	21.471	3.186	0.0007	21.4717	21.459	-0.0127
20.11	22.480	4.195	0.0015	22.4815	22.467	-0.0145
20.12	23.520	5.235	0.0028	23.5228	23.505	-0.0178
20.15	24.478	6.193	0.0042	24.4822	24.469	-0.0132
20.16	25.460	7.175	0.0060	25.4660	25.452	-0.0140
20.10	26.013	7.730	0.0073	26.0203	26.006	-0.0143
20.20	27.048	8.763	0.0096	27.0576	27.045	-0.0126

*resolution to 0.0001°C

s = average surrounding temperature over a period of 1 hr.

tu = Mercury thermometer (N.P.L.B.S. 791 type)

t = Mercury thermometer (N.P.L.B.S. 791 type) corrected. (Exposed stem correction, E.S.C.)

E.S.C. = $1.6 \times 10^{-4} \times H\ (tu - S)$

H = exposed mercury stem height (ESH, in °C)

Q = Z - 0.01, corrected Quartz temperature (°C)

Z = Uncorrected Quartz temperature (°C)

n = difference in temperatures (°C)

CALIBRATION OF MERCURY THERMOMETER AGAINST QUARTZ THERMOMETER(2801A,HEWLETT PACKARD)

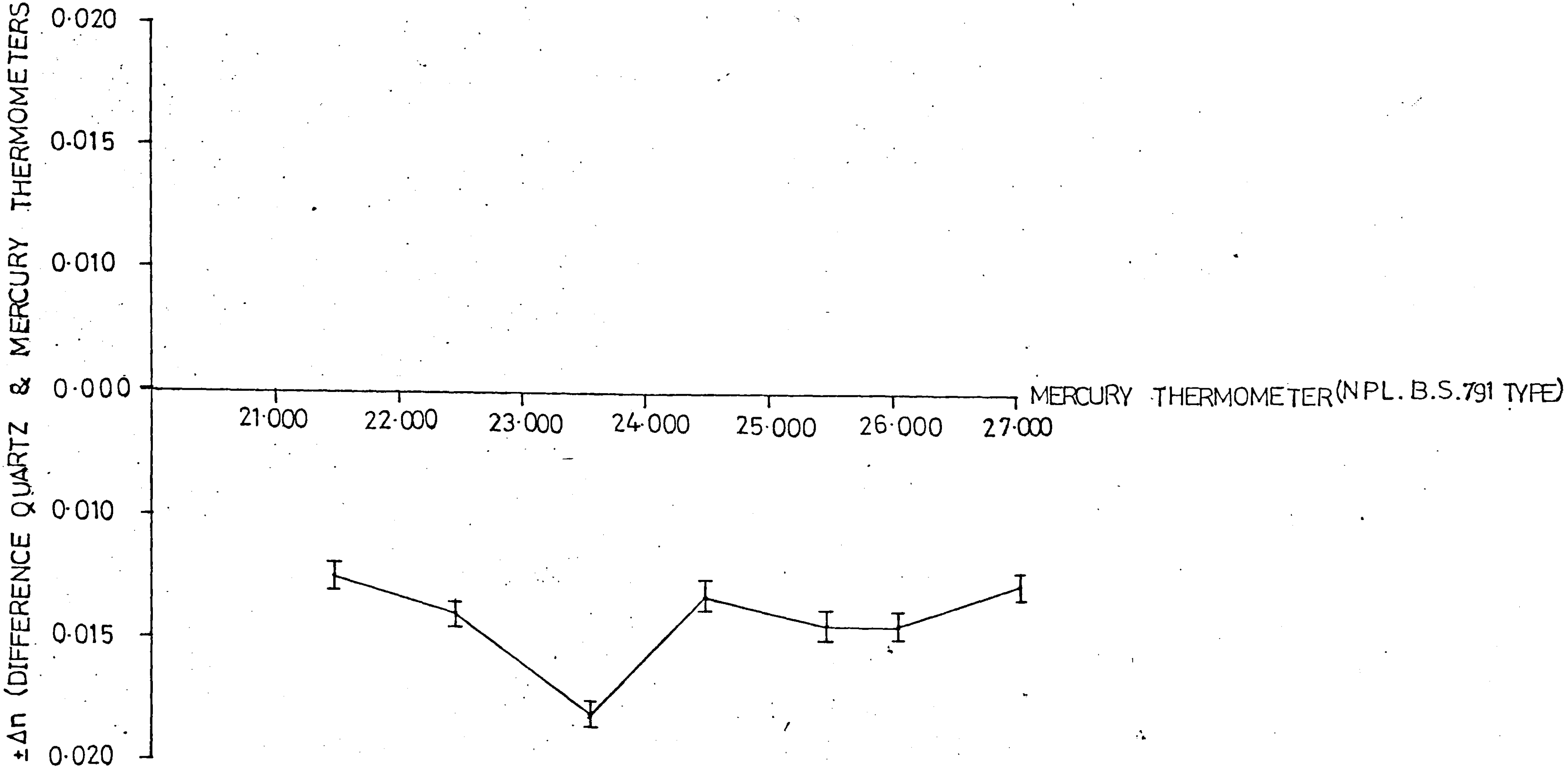


Fig. <u>Absolute temperature error(Δn) of Mercury in glass thermometer Vs. apparent temperature.</u>

TABLE Comparison of Vapour Pressure Data for Ferrocene (See graph on P. 185)

EDWARDS and KINGTON [196]				ANDREWS and WESTRUM [200]				THIS WORK [76]			
T (^oK)	$10^3/T$ (^oK)	10^3 P (mm.Hg.)	$3+\log_{10}P$	T (^oK)	$10^3/T$ (^oK)	10^3 P (mm.Hg.)	$3+\log_{10}P$	T (^oK)	$10^3/T$ (^oK)	10^3 P (mm.Hg.)	$3+\log_{10}P$
295.039	3.389	5.129	0.7101	294	3.401	4.686	0.6708	294.137	3.399	4.872	0.6877
295.082	3.389	5.165	0.7131	295	3.390	5.291	0.7235	295.134$_5$	3.388	5.165	0.7131
298.004	3.356	6.908	0.8393	296	3.378	5.848	0.7670	296.132	3.377	5.829	0.7656
298.007	3.356	6.894	0.8385	297.	3.367	6.459	0.8102	297.134	3.365	6.549	0.8161
298.007	3.356	6.897	0.8386	298	3.356	7.136	0.8534	298.136	3.354	6.795	0.8322
300.345	3.329	8.730	0.9410	299	3.344	7.865	0.8957	299.136	3.343	7.929	0.8992
300.314	3.330	8.694	0.9392	300	3.333	8.676	0.9383	300.137	3.332	8.926	0.9506
303.056	3.299	11.174	1.0482	301	3.322	9.550	0.9800				
303.073	3.299	11226	1.0500	302	3.311	1.052	1.0220				
				303	3.300	1.212	1.0835				
				304	3.289	1.272	1.1045				
				305	3.278	1.397	1.1452				

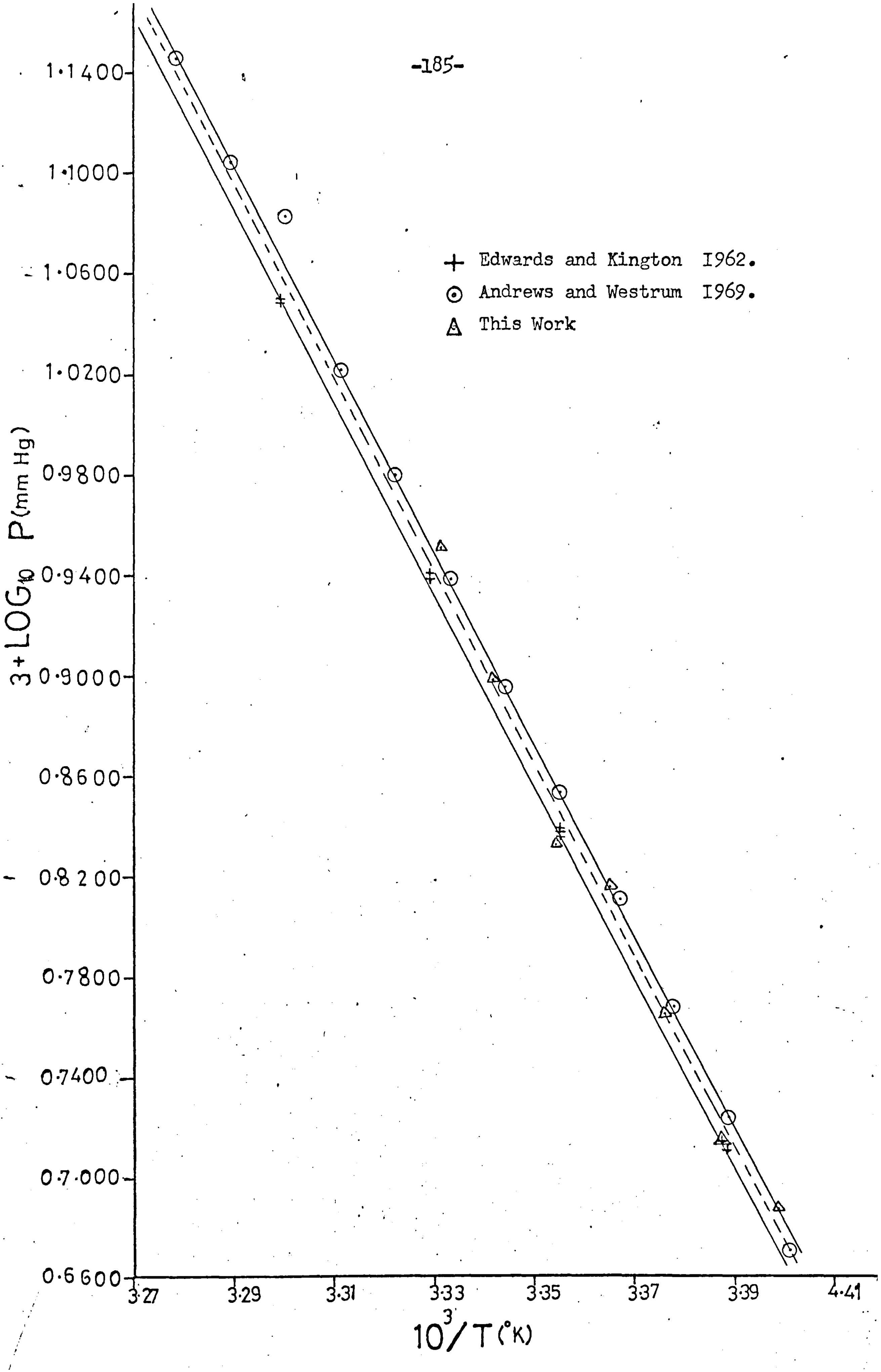


Fig. Comparison of Vapour Pressure Data for Ferrocene.

TABLE Effusion Manometric Results for Ferrocene $(C_5H_5)_2Fe$

λ = Free-mean path = $(\sqrt{2}\,\pi N d^2)^{-1}$, N = number density, $\overline{P} = \frac{1}{2}(P_{(1)} + P_{(2)})$ [See pp.100-3 for the expressions.]

d = effective collision diameter with Vander Waals radii (7.36°A) P = $P_{(3)} = P_{(2)}$ XF (F = Hiby and Pahl correction factor)

W/t (g, Sec^{-1})	T (°K)	$10^3/T$(°K)	$10^3\,\overline{P}$ (mm.Hg.)	$10\,\lambda$ (cm.)	F	10^3 P (mm.Hg.)	$3 + \log_{10}P$
0.0168/72000	294.137	3.399	4.998	2.542	0.9828	4.872	0.6877
0.0178/72000	295.134$_5$	3.388	5.304	2.404	0.9819	5.165	0.7131
0.0201/72000	296.132	3.377	5.999	2.132	0.9796	5.829	0.7656
0.0226/72000	297.134	3.365	6.757	1.899	0.9771	6.549	0.8161
0.0246/75600	298.136	3.354	7.017	1.835	0.9764	6.795	0.8322
0.0274/72000	299.136	3.343	8.220	1.572	0.9725	7.929	0.8992
0.0309/72000	300.137	3.332	9.285	1.396	0.9692	8.926	0.9506

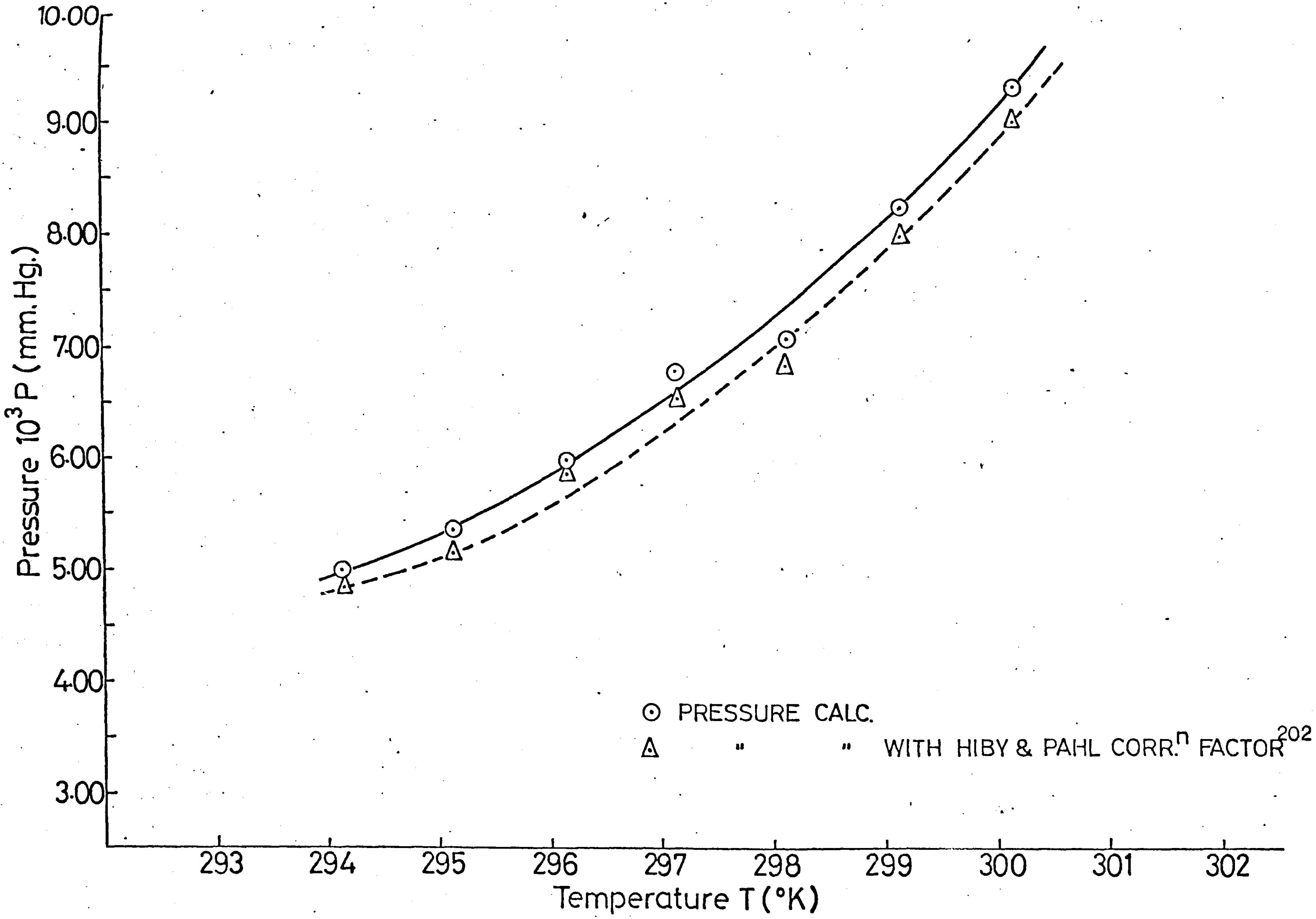


Fig. Vapour Pressure vs. Absolute Temperature for Ferrocene.

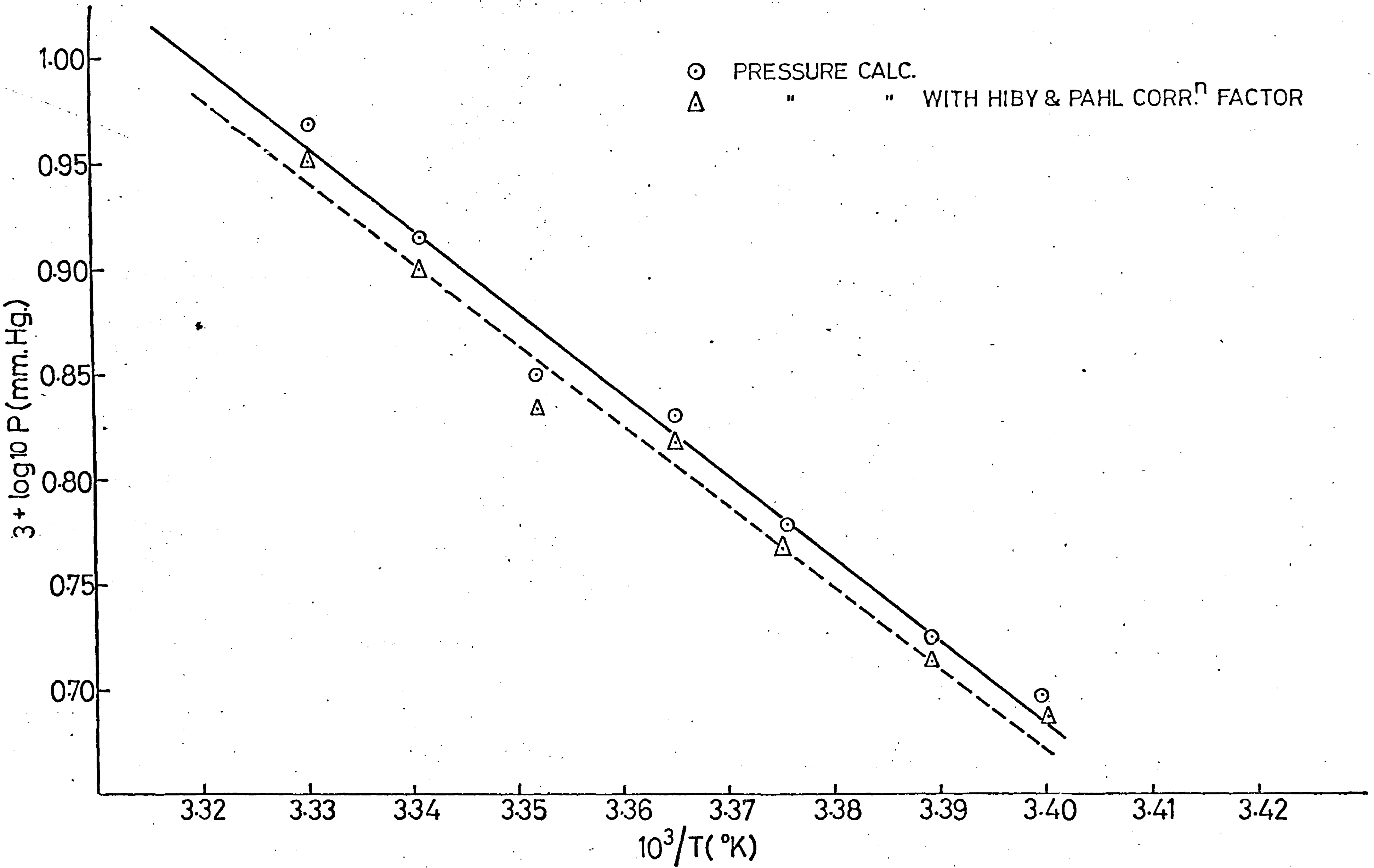


Fig. Logarithm of Vapour Pressure vs. Reciprocal Absolute Temperature for Ferrocene.

TABLE Effusion Manometric Results for PI_3

λ = Free-mean path = $(\sqrt{2}\pi N d^2)^{-1}$, N = number density, $\overline{P} = \frac{1}{2}(P_{(1)} + P_{(2)})$ (See pp.100-3 for the expressions)

d = effective collision diameter with Vander Waals radii (8.56°A), $P = P_{(3)} = P_{(2)} \times F$ (F = Hiby and Pahl correction factor)

W/t (g. Sec^{-1})	T (°K)	$10^3/T$ (°K)	$10^3 \overline{P}$ (mm.Hg.)	$(\frac{10\lambda}{cm})$	F	10^3 P (mm.Hg.)	3 + $\log_{10}P$
0.0135/72000	294.137	3.399	2.690	3.492_5	0.9874	2.634	0.4206
0.0135/72000	294.137	3.399	2.690	3.492_5	0.9874	2.634	0.4206
0.0143/72000	295.134_5	3.388	2.854	3.303	0.9867	2.793	0.4460
0.0152/72000	295.134_5	3.388	3.034	3.107	0.9859	2.966	0.4722
0.0166/72000	296.132	3.377	3.319	2.850	0.9847	3.241	0.5106
0.0166/72000	296.132	3.377	3.318	2.850	0.9847	3.241	0.5106
0.0171/72000	297.134	3.365	3.424	2.771	0.9842	3.343	0.5241
0.0174/72000	297.134	3.365	3.484	2.724	0.9839	3.400	0.5315
0.0206/72000	298.136	3.354	4.132	2.304	0.9811	4.021	0.6043
0.0194/72000	298.136	3.354	3.891	2.447	0.9822	3.791	0.5787
0.0204/72000	299.136	3.343	4.099	2.331	0.9813	3.989	0.6009
0.0225/72000	300.137	3.332	4.528	2.117	0.9795	4.399	0.6433

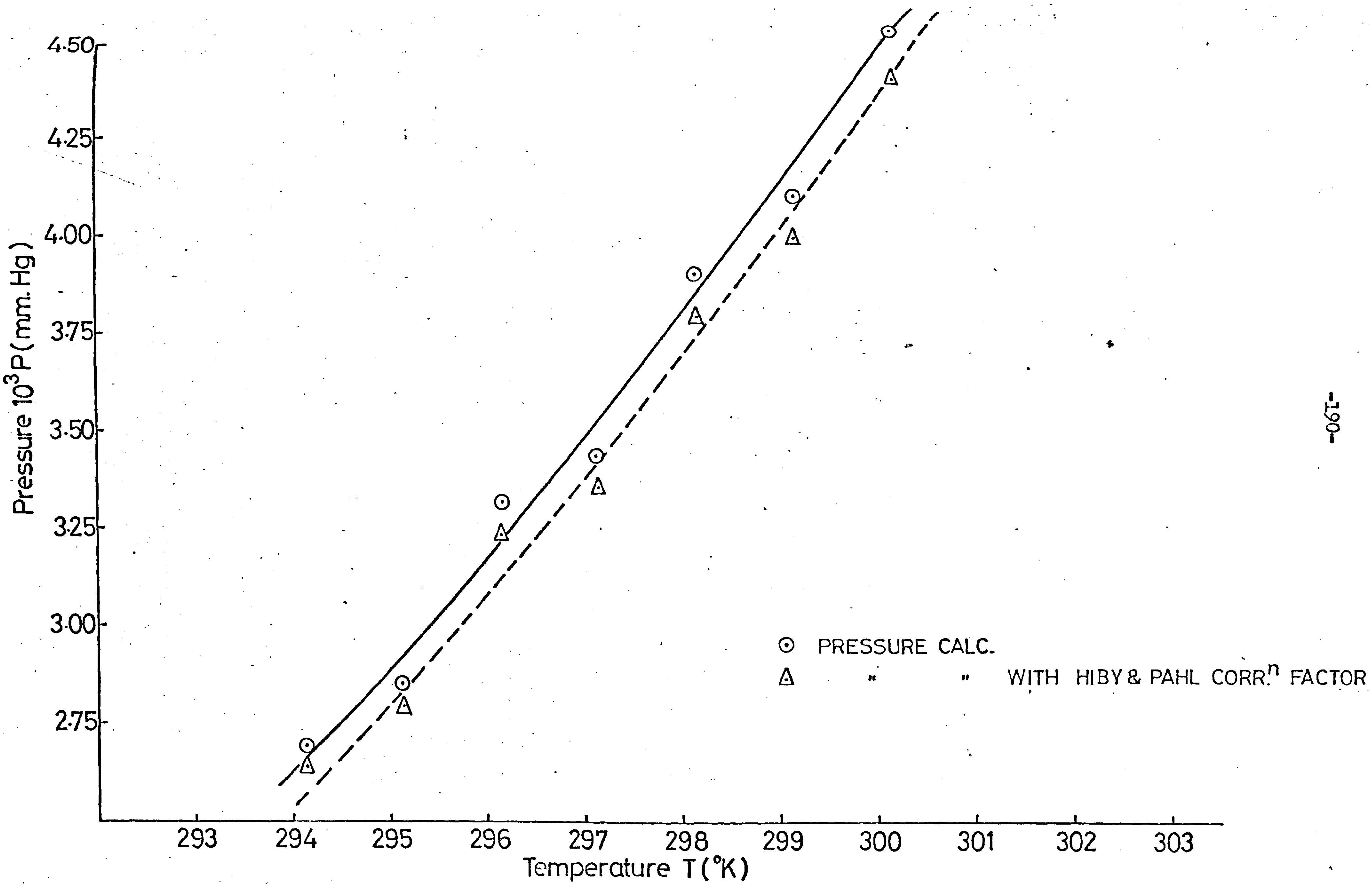


Fig. Vapour Pressure vs. Absolute Temperature for Triiodophosphine.

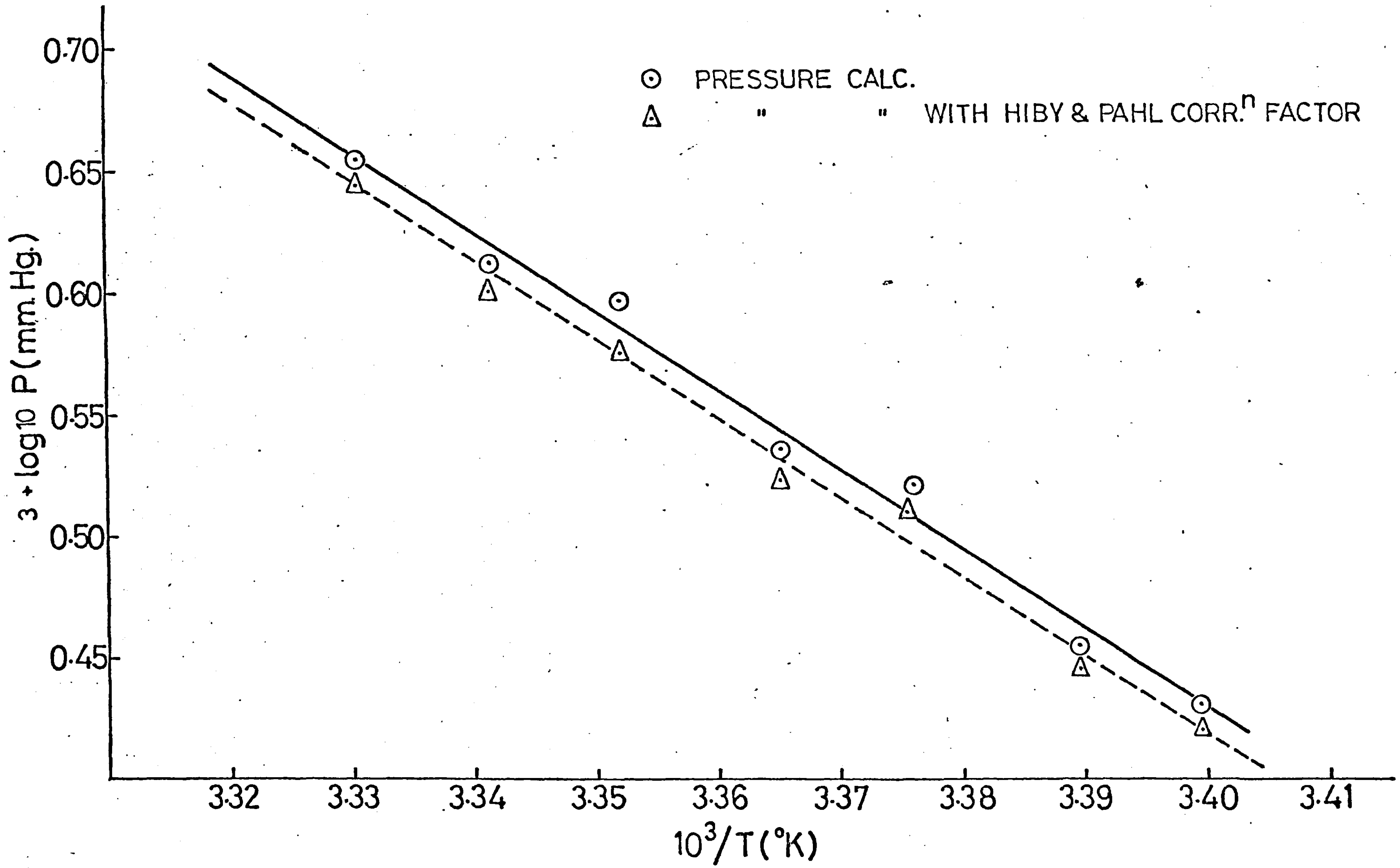


Fig. Logarithm of Vapour Pressure vs. Reciprocal Absolute Temperature for Triiodophosphine.

TABLE Effusion Manometric Results for P_2I_4

λ = Free-mean path = $(\sqrt{2}\pi N d^2)^{-1}$, N = number density, $\overline{P} = \frac{1}{2}(P_{(1)} + P_{(2)})$ (See pp.100-3 for the expressions)

d = effective collision diameter with Vander Waals radii (9.85 Å), $P = P_{(3)} = P_{(2)} \times F$ (F = Hiby and Pahl correction factor)

W/t ($g.\ Sec^{-1}$)	T (^oK)	$10^3/T$	$10^3\ \overline{P}$ (mm.Hg.)	10λ (cm.)	F	$10^3\ P$ (mm.Hg.)	$3 + \log_{10}P$
0.0113/86400	328.09	3.048	1.690	4.682	0.9906	1.661	0.2203
0.0111/86400	328.09	3.048	1.660	4.766	0.9907	1.632	0.2126
0.0110/86400	328.09	3.048	1.645	4.809	0.9908	1.617	0.2087
0.0129/86400	330.09	3.030	1.935	4.113	0.9893	1.899	0.2786
0.0129/86400	331.09	3.020	1.938	4.119	0.9893	1.902	0.2792
0.0150/86400	333.08	3.002	2.261	3.553	0.9876	2.215	0.3453
0.0148/86400	333.08	3.002	2.231	3.601	0.9878	2.186	0.3395
0.0149/86400	333.08	3.002	2.246	3.577	0.9877	2.200	0.3424
0.0148/86400	333.08	3.002	2.231	3.601	0.9878	2.186	0.3395
0.0226/86400	338.06	2.958	3.432	2.376	0.9816	3.341	0.5239
0.0224/86400	338.06	2.958	3.401	2.397	0.9818	3.312	0.5201
0.0318/86400	343.04	2.915	4.864	1.701	0.9746	4.702	0.6722
0.0303/86400	343.04	2.915	4.635	1.785	0.9757	4.485	0.6518
0.0304/86400	343.04	2.915	4.650	1.779	0.9756	4.500	0.6532
0.0302/86400	343.04	2.915	4.620	1.791	0.9758	4.471	0.6504
0.0300/86400	343.04	2.915	4.589	1.803	0.9760	4.442	0.6476
0.0430/86400	348.02	2.873	6.625	1.267	0.9662	6.349	0.8026
0.0798/86400	353.00	2.833	12.383	0.6876	0.9394	11.536	1.0620

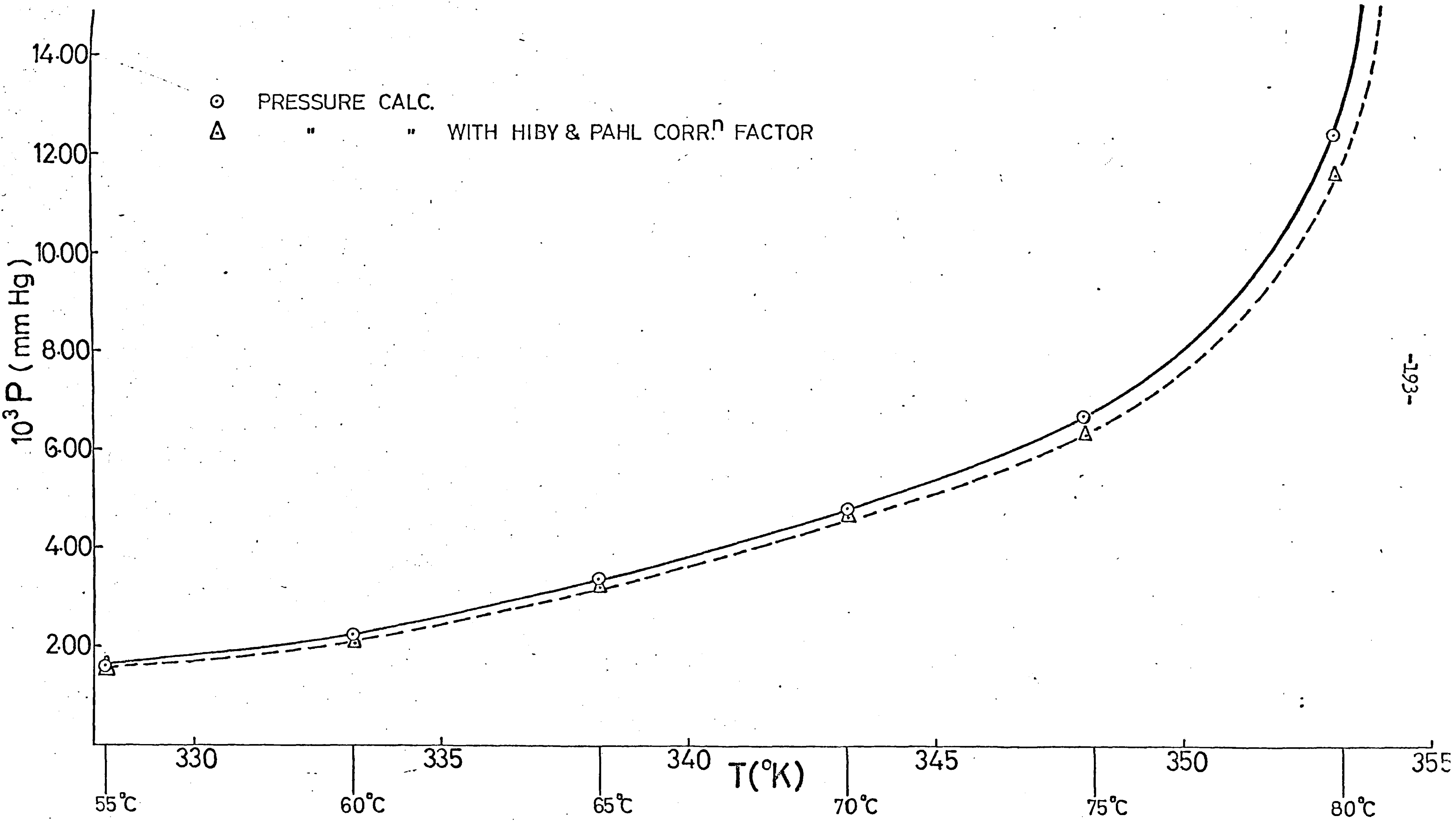


Fig. Vapour Pressure vs. Absolute Temperature for Phosphorus Tetraiodide.

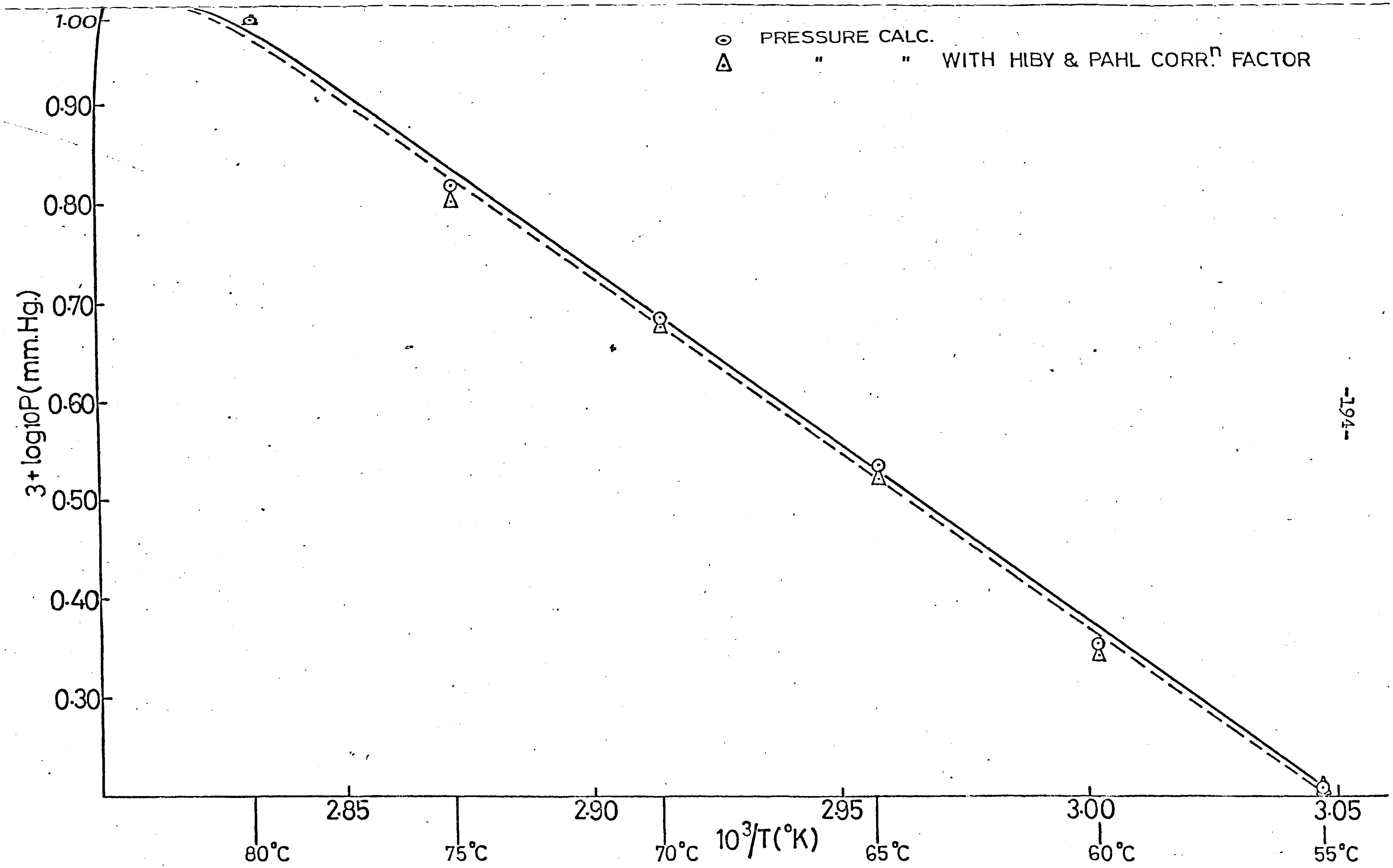


Fig. Logarithm of Vapour Pressure vs. Reciprocal Absolute Temperature for Diphosphorus Tetraiodide.

SECTION-IV. DISCUSSION

CHAPTER TEN:

DISCUSSION

The Phosphorus-Phosphorus Bond Strength in Diphosphorus tetraiodide

Bond energies and bond dissociation energies are usually derived from thermochemical[12,25,29,32,35,36,213] and mass-spectrometric[25,41,187,190,213] measurements respectively. These procedures are adopted in the present investigation for the determination of the bond energy, E_{P-P}, and the bond dissociation energy, D_{P-P}, in diphosphorus tetraiodide. The ancillary data required for the determination of E_{P-P} can be seen from the following thermodynamic equations.

$$P_2I_4(g) = 2P(g) + 4I(g)$$

$$\therefore E_{P-P} + 4E_{P-I} = 2\ \Delta H_f^o(P,g) + 4\ \Delta H_f^o(I,g) - \Delta H_f^o(P_2I_4,g)$$

There is no direct method for the determination of the phosphorus-iodine bond in diphosphorus tetraiodide, hence the assumption is made that E_{P-I} in diphosphorus tetraiodide equals $\bar{E}_{P-I}$ in triiodophosphine. This also presumes a knowledge of the standard heat of formation of triiodophosphine (gas). Data for the standard heat of formation of diphosphorus tetraiodide (crystal) and triiodophosphine (crystal) are now available in the literature,[104] but no experimental data for the latent heats of sublimation of triiodophosphine or diphosphorus tetraiodide were available in the literature. Therefore these have been determined via an effusion manometric technique. A full description of this technique appears in Chapter five. Previously estimates for these functions have been made. For example, the latent heat of sublimation of diphosphorus tetraiodide was estimated as 30 Kcal $mole^{-1}$ in 1940. Doubts have been expressed as to the magnitude of this estimate.[32] This investigation now shows that the sublimation enthalpy is 16.70 ± 0.5 Kcal $mole^{-1}$, much lower than the estimate.

(See Chapter nine: Effusion Manometric Results, for further details). Sublimation enthalpies are always the most difficultly-accessible functions in the determination of bond energies in compounds whose standard states are crystalline and which melt with decomposition. Therefore the thermal stability of diphosphorus tetraiodide has been investigated by a thermal analysis technique (see Chapter four: (A)). Results obtained from thermogravimetric analysis (TGA) show a negligibly small (ca. 3%) weight-loss prior to the melting point, which is presumably due to sublimed material escaping from volatile sample cell. (See Chapter seven: Thermal Analysis Results for design of cell and full details of TGA). For substances having low vapour pressures,[203] less than 0.05 mm. Hg. at ambient temperature, effusion manometry is a suitable technique for vapour pressure determination. An effusion manometer similar to the design of Edwards and Kington[196] has been constructed for this work (see Chapter five: Effusion Manometry, for design and description of the manometer). A minor modification in the material of the effusion cell was introduced due to the corrosive nature of the phosphorus iodides. The effusion cell is fabricated in stainless steel and the foil in gold. Initially the effusion manometer was tested with a carefully purified sample of ferrocene. The purification procedure of Edwards[167] et al. was used (see Chapter two: Purification). The fundamental quantity measured by an effusion manometer is vapour pressure. There are two sets of reliable data in the literature for ferrocene, using a similar manometer and temperature range. The present results for the vapour pressure of ferrocene are in excellent agreement with Edwards and Kington. (See Chapter nine: Effusion Manometric Results, for numerical data and graphs).

Table - Comparison of Effusion Manometric Data for Ferrocene

INVESTIGATOR	MATERIAL		VAPOUR PRESSURE 298°K (mm. Hg.)	$\Delta H_{(c\to g)}$ 298°K (Kcal mole^{-1})	$\Delta H_{(c\to g)}$ 298°K (KJ mole^{-1})
	EFFUSION CELL	FOIL			
Edwards and Kington[196]	Aluminium	Copper	0.00684	17.53 ± 0.10	73.34 ± 0.42
Andrews and Westrum[200]	Copper	Copper	0.00714	17.38 ± 0.13	72.72 ± 0.54
This Work	Stainless Steel	Gold	0.00680	17.84 ± 0.96	74.64 ± 4.02

The value of the enthalpy of sublimation of ferrocene, listed in the above table, is derived from the Clausius-Clapeyron equation. There is nearly an order of magnitude difference in precision of the present data compared with that of Edwards and Kington or Andrews and Westrum. This may be attributed to the necessity of fabricating the effusion cell in stainless steel, a relatively poor thermal conductor[215] compared with copper or aluminium (Cu, 3.85: Al, 2.38: stainless steel, 0.245 Joule cm. cm^{-2} sec^{-1}deg^{-1} at 0°C). Using this apparatus, the vapour pressure of triiodophosphine and diphosphorus tetraiodide were determined. These compounds are oxygen- and moisture-sensitive, so appropriate precautions were taken in their handling. Triiodophosphine was studied over the temperature range 20-28°C and diphosphorus tetraiodide over a higher range, 50-80°C. This is because preliminary experiments for this compound gave irreproducibly small weight losses. Each run over the same temperature range was repeated thrice in ascending and descending order of temperature. The sublimate of triiodophosphine and diphosphorus tetraiodide in isolated runs was analysed. In both cases the theoretical I:P ratio was confirmed. Also the absolute weight loss in isolated runs was confirmed by analysis of the sublimate. The correction to be applied for conversion of the diphosphorus tetraiodide data (observed at 340°K) to 298.15°K is assumed to be within the experimental limits of error. Least-squares analysis gave (see Chapter nine: Effusion Manometric Results, for complete numerical and graph details).

$$\Delta H\ (PI_3,\ c\rightarrow g)\ 298 = 15.21 \pm 0.86\ \text{Kcal mole}^{-1}$$

$$\Delta H\ (P_2I_4,\ c\rightarrow g)\ 298 = 16.70 \pm 0.50\ \text{Kcal mole}^{-1}$$

Incorporating the first figure in a thermodynamic cycle for triiodophosphine along with ancillary data (as shown on p. 200), the average bond dissociation energy, $\bar{E}_{P-I}$ is obtained as 50 Kcal mole^{-1}. This figure, assumed equal to E_{P-I} in diphosphorus tetraiodide, is inserted into a similar cycle for diphosphorus tetraiodide and a value of 62 Kcal[76,214] has resulted for bond energy E_{P-P}.

Most phosphorus-phosphorus bonded compounds (acyclic and cyclic) have a nearly constant P-P bond length of ca. 2.21°A. Some of these are listed below with exceptions.

Table - Phosphorus-Phosphorus Bond Lengths

COMPOUND	PHASE STUDIED	METHOD	P-P BOND LENGTH (°A)	REF.
P_2I_4	Solid	X-ray	2.21 ± 0.06	95
$P_2(CH_3)_4$	Gas	Electron Diffraction	2.190 ± 0.009	216
P_4	Gas	Electron Diffraction	2.21 ± 0.02	217
$(CF_3P)_4$	Solid	X-ray	2.210 ± 0.005	218
$(C_6H_5P)_5$	Solid	X-ray	2.210 ± 0.006	78
$(C_6H_5P)_6$	Solid	X-ray	2.230 ± 0.005	79

In contrast, the data concerning phosphorus-phosphorus bond energy E_{P-P} and bond dissociation energy D_{P-P} are divergent. These appear in the following table.

$$\begin{tikzcd}
PI_3(c) \arrow[r, "(2)"] & PI_3(g) \arrow[d, "(3)"] \\
\frac{1}{4}P_{4(c)} + \frac{3}{2}I_{2(c)} \arrow[u, "(1)"] \arrow[r, "(4)"'] & P(g) + 3I(g)
\end{tikzcd}$$

$$\begin{tikzcd}
P_2I_4(c) \arrow[r, "(2)"] & P_2I_4(g) \arrow[d, "(3)"] \\
\frac{1}{2}P_{4(c)} + \frac{4}{2}I_{2(c)} \arrow[u, "(1)"] \arrow[r, "(4)"'] & 2P(g) + 4I(g)
\end{tikzcd}$$

Kcal(x4·184=KJ)

(1) $\Delta H^{o}_{f}\ PI_3$ = $-14\cdot17 \pm 0\cdot60$ (Lit.)[32,89]

(2) $\Delta H_{sub.}PI_3$ = $15\cdot21 \pm 0\cdot86$ (This work)
 30 (Estimated)[105]

(3) $3\bar{E}_{P-I}$ = 150·76 (Calc.)
or
$\bar{E}_{P-I}$ = 50·25 (Calc.)

(4) $\Delta H_{atom.}$ = 151·80 (Lit.)[32,210]

Kcal(x4·184=KJ)

(1) $\Delta H^{o}_{f}\ P_2I_4$ = $-27\cdot03 \pm 1\cdot19$ (Lit.)[104]

(2) $\Delta H_{sub.}P_2I_4$ = $16\cdot70 \pm 0\cdot50$ (This work)

(3) E_{P-P} = 61·87 (Calc.)
+
$4E_{P-I}$ = 201·00 (Calc.)

(4) $\Delta H_{atom.}$ = 252·54 (Lit.)[32,210]

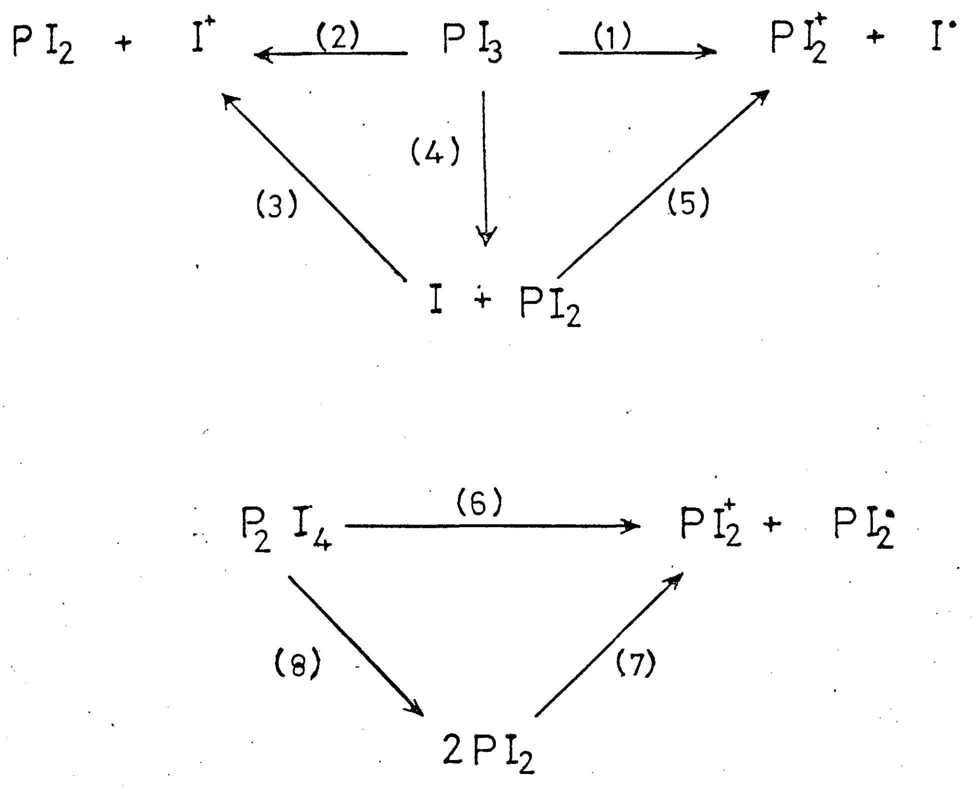
$\bar{E}_{P-I}$ = E_{P-I} (Assumed)

Fig. Thermodynamic cycles, for average bond dissociation energy of phosphorus iodide bonds in triiodophosphine and for bond energy of phosphorus-phosphorus bond in diphosphorus tetraiodide using Thermochemical and Effusion manometric Data.

COMPOUND	THERMODYNAMIC FUNCTION		REF.
	E_{P-P}	D_{P-P}	
P_2H_4	47	74,74	73,219,220
P_2I_4	62		This Work
	67 (estimated)		32
P_2Cl_4		58	74
$P_2(C_2H_5)_4$		86	221
P_4	51 (estimated)		8

The extent of the participation of the 3s, 3p and 3d orbitals in the P-P bond remains unsettled.[1,8,23,52,54,58,64,68] Hence energetic calculations based on the electronic character of the bond are not yet meaningful.

From comparison of the relative percentage abundances in the mass spectra of diphosphorus tetrafluoride and dinitrogen tetrafluoride, it has been suggested[222] that the P-P bond strength is greater than N-N bond strength. Appearance potential measurements for the phosphorus-chloride[74] system (PCl_3 and P_2Cl_4) have shown that D_{P-P} in diphosphorus tetrachloride is ca. 58 Kcal mole^{-1}. In this work, the phosphorus-iodide system has been investigated by a similar technique to obtain D_{P-P} in diphosphorus tetraiodide. (See Chapter four: (B) for Mass Spectrometric technique and Chapter eight: Mass Spectrometric Results for complete details of the mass spectra). The determination of D_{P-P} in diphosphorus tetraiodide requires a knowledge of the ionization potential I.P.(PI_2) in P_2I_4 and the appearance potential A.P.(PI_2^+) for P_2I_4 species. Both these values are not available in the literature. Therefore A.P.(PI_2^+) for P_2I_4 was experimentally measured in this work using an AEI model MS2H mass spectrometer with a direct inlet system for solid samples. The method of Lossing[194] et al. was



D(B.DE) = BOND DISSOCIATION ENERGY

A.P. = APPEARANCE POTENTIAL

I.P. = IONIZATION POTENTIAL

[eV]

(1) A.P. $(PI_2^+)_{PI_3}$ = 11·9 ± 0·15 (This work)

(2) A.P. $(I^+)_{PI_3}$ = 12·7 ± 0·15 [Assumed, $\simeq \bar{E}_{P-I}$ + I.P.(I)]

(3) I.P. (I) = 10·45 (Lit.)[223]

(4) D_{I_2P-I} = 2·25 (Calc.)

(5) I.P. (PI_2) = 9·65 (Calc.)

(6) A.P. $(PI_2^+)_{P_2I_4}$ = 12·8 ± 0·15 (This work)

(7) I.P. (PI_2) = 9·65 [Calc. as in (5)]

(8) $D_{I_2P-PI_2}$ = 3·15 ± 0·26 (Calc.)

Fig. Thermodynamic cycles for bond dissociation energies of phosphorus iodide bond in triiodophosphine and of phosphorus-phosphorus bond in diphosphorus tetraiodide using Mass Spectrometric Data.

employed to determine the appearance potential using argon as internal standard.

$$P_2I_4 + e \longrightarrow PI_2^+ + PI_2 + 2e \qquad A.P.(PI_2^+)_{P_2I_4} = 12.8 \pm 0.15eV$$

Since there are no data available in the literature for $I.P.(PI_2)$ from P_2I_4, an indirect method can be used by equating this function via $I.P.(PI_2)$ from PI_3. $I.P.(I) = 10.45eV$ [223], but $A.P.(PI_2^+)_{PI_3}$, $A.P.(I^+)_{PI_3}$ and D_{I_2P-I} are unknown. The experimental measurement of $A.P.(PI_2^+)$ for PI_3 in the present work was performed using the same instrument and adopting similar procedure as for P_2I_4. The process investigated under electron impacts was

$$PI_3 + e \longrightarrow PI_2^+ + I + 2e \qquad A.P.(PI_2^+)_{PI_3} = 11.9 \pm 0.15eV$$

The further assumption is made that $D_{I_2P-I} = \bar{E}_{I_2P-I}$ in triiodophosphine, and hence, inserting the relevant values, it follows that D_{P-P} in diphosphorus tetraiodide is 72.60 ± 6 Kcal mole^{-1}. This must be considered as an upper limit [25] in view of the kinetic energy imparted to the fragment-ion by the accelerating voltage.

Phosphobenzene

The tendency towards catenation[1] rather than to multiple bonding in phosphorus compounds is demonstrated in the synthesis of mono-, bi-, tri, and polycyclic compounds (see Appendix six: Classification, for illustrations). This fact, as with other members of the second period may be attributed to increased inner shell repulsion and reluctance[224] to form $p\pi$ bonds. The term phosphobenzene comprises groups of compounds which readily interconvert[85] in solution. Some forms, identified as stable crystals under atmospheric conditions, are homocyclic, e.g. pentaphenylcyclopentaphosphine, hexaphenylcyclohexaphosphine and the so-called polymeric phenylphosphine. There seem to be unusual difficulties associated with the methods of synthesis in the above compounds, and as a result, no reproducible routes are available. Hexameric phosphobenzene is known to exist in four different allotropic modifications[85] i.e. monoclinic, triclinic, trigonal and hexagonal (see Chapter one, for hexameric trigonal structure). In the present work synthetic methods for these compounds have been investigated. For the pentamer, a method based on the following reaction has proved to be the most reliable and reproducible.

$$5C_6H_5PCl_2 + 5(C_4H_9)_3P^{[7]} = (C_6H_5P)_5 + 5(C_4H_9)_3PCl_2$$

The reaction takes approximately 20 min. to complete, rather than a few seconds as reported in literature. Further, this reference quotes the product as tetrameric. This material has now been identified as the pentamer by comparison of the interplanar spacings obtained via X-ray analysis with that of an authentic sample of pentaphenylcyclopentaphosphine. The numerical data and intensity estimation are presented in Appendix four. The melting-point and the purity of the material has been established via DSC and DTA methods (see Chapter four (A)). The results indicate that pentaphenylcyclopentaphosphine is pure from the characteristic sharp melting point peak at 154°C (see Chapter seven: Thermal Analysis Results). Confirmation of purity of this material was also obtained by microanalysis. It can be seen that the material is 99.0% pure based on C_6H_5P. The I.R. and Raman spectra show some different features compared to the then-called tetramer.[77] (See Appendix three).

Repeated attempts to synthesise hexaphenylcyclohexaphosphine by literature methods have failed in the present investigation. It appears that interconversion in this form of phosphobenzene is very facile. Also low thermal stability within the allotropic modifications is manifested. For example, a change in crystal habit of an authentic sample of hexamer was observed (also noted by Maier).[225] This was the conversion of transparent trigonal to milky triclinic. The possibility of atmospheric oxidation was excluded as the crystals were stored in dry nitrogen. The exact conditions for interconversion are not yet completely understood. (See Chapter one: for interconversion scheme). A method suggested for the synthesis of polymeric phenylphosphine via warming the pentamer in piperidine at 80°C did not produce satisfactory results after repeated attempts. Hence a direct synthetic route[153] for the polymeric substance was investigated. This is based on the disproportionation reaction of phenyldifluorophosphine. The same reaction[226] has been reported to yield form A (m.pt. 151-154°C), this was confirmed by X-ray analysis. The proposed disproportionaction reaction was

$$10C_6H_5PF_2 \longrightarrow 5C_6H_5PF_4 + (C_6H_5P)_5$$

In the present work, however, the polymeric phenylphosphine was produced. The initial reaction shown below proceeds in sulpholane at 100°C, followed by disproportionation of phenyldifluorophosphine at room temperature after nine hours standing.

$$C_6H_5PCl_2 + 2NaF = C_6H_5PF_2 + 2NaCl$$

$$2C_6H_5PF_2 = C_6H_5PF_4 + \frac{1}{n}(C_6H_5P)_n$$

The resulting material had a m.pt. range 264-280°C (sealed tube) compared with the literature[61,62] m.pt. for C and D of 252-285°C. Confirmation was obtained by comparison of the X-ray diffraction pattern with that of an authentic sample (from Maier). The comparison showed minor differences in both intensities and interplanar spacings but eliminated the possibility of form A. The disproportionation of phenyldifluorophosphine in the presence of phenyldichlorophosphine under nitrogen also gives polymeric phenylphosphine.

There are no thermodynamic data for phosphobenzene at present in the literature. The thermochemical results obtained in this investigation were achieved by reaction-solution calorimetry (see Chapter three and Chapter six) and thermal analysis (see Chapter four (A) and Chapter seven). In order that any reaction be studied thermodynamically it is essential that its stoichiometry be known exactly. Stoichiometric reactions of pentameric and polymeric phosphobenzene to phenyldibromophosphine and phenyltetrabromophosphorane have been established (see Chapter six: Thermochemical Results) by bromine oxidation in non-aqueous solvents.

$$(C_6H_5P)_5(\text{cryst.}) + 5Br_2(\text{in } C_6H_6) = 5C_6H_5PBr_2(\text{in } C_6H_6)$$

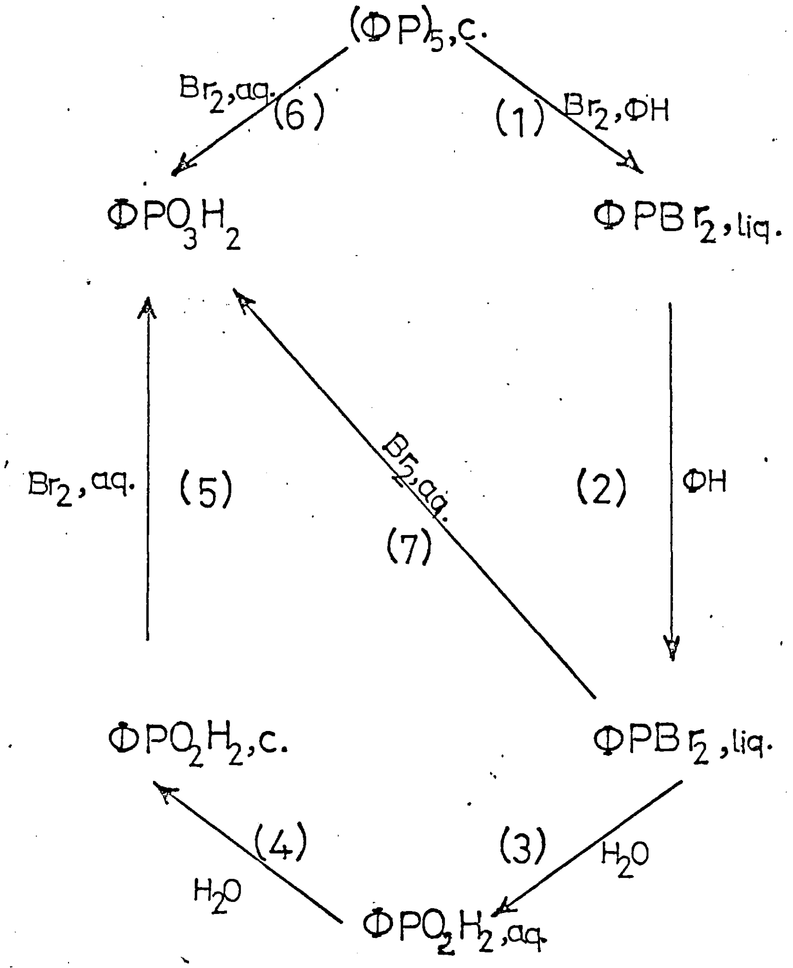
$$\frac{1}{n}(C_6H_5P)_n(\text{cryst.}) + 2Br_2(\text{in } C_6H_6) = C_6H_5PBr_4(\text{in } C_6H_6)$$

The fundamental quantity usually measurable by reaction-solution calorimetry is the heat of reaction, and the thermodynamically significant quantity derivable is the standard heat of formation, ΔH^of. For phosphobenzene (pentamer and polymer), heats of reaction are measured in this work which would be useful in deriving standard heat of formation of the pentamer when ancillary thermodynamic data are available (see Chapter six). These are the standard heat of formation for phenylphosphonous and phenylphosphonic acids. The reactions studied calorimetrically for pentaphenylcyclopentaphosphine are shown in the thermodynamic cycle on p. 208 Details of the thermodynamic equations and the corresponding enthalpies are shown in Chapter six. The discrepancy of 1.80 Kcal has appeared in the present cycle for pentaphenylcyclopentaphosphine. This error probably occurs in the slow reaction (step (6)) in the first half of the cycle. That the second half of the cycle is self-consistent is shown by the excellent agreement between steps (3), (4) and (5), and step (7).

Phase change studies in solids are most conveniently conducted by DSC or DTA methods . Qualitative analysis of the thermograms (DSC and DTA) obtained for phosphobenzene indicate the following phase changes (recorded on a temperature-increasing programme).

PHOSPHOBENZENE	TRANSITION TEMPERATURE (°C)	
	PHASE CHANGE (exothermic)	MELTING (endothermic)
$(C_6H_5P)_5$	86	154
$(C_6H_5P)_6$	76 and 130	190
$(C_6H_5P)_n$	86	285

Calibration with an indium standard indicates these temperatures are accurate to ± 0.5°C. No phase changes are noted on recycling any of these samples. Presumably, therefore, solidification on cooling to ambient temperature under calorimetric conditions did not occur. Quantitative measurements for the enthalpy change at fusion have been made for the pentamer and the polymeric form (with reference to an indium standard). The thermogram (DSC) for the polymeric form was analysed to determine the crystallinity of the sample,



$\Delta H_{obs.}$ Kcal (x4·184 = KJ)

(1)	$-28{\cdot}64 \pm 0{\cdot}35$	(4)	$-1{\cdot}43 \pm 0{\cdot}04$
(2)	$+0{\cdot}58 \pm 0{\cdot}01$	(5)	$-61{\cdot}31 \pm 0{\cdot}33$
(3)	$-41{\cdot}7 \pm 0{\cdot}08$	(6)	$-133{\cdot}48 \pm 0{\cdot}32$
		(7)	$-104{\cdot}36 \pm 0{\cdot}13$

$$\Delta H\ (6) - \sum_{1}^{5} \Delta H = \Delta H_f^{\circ}[Br_2\ ,aq.] - \Delta H_f^{\circ}[Br_2\ ,\Phi H]$$

Fig. Thermodynamic cycle for pentaphenylcyclopentaphosphine compared to a polyethylene[49] reference. The result shows ca. 73% crystallinity in polymeric phenylphosphine and suggests heterogeneity (see Chapter seven: Thermal Analysis for details). The literature records only one crystalline form for the pentamer, so the transition at 86° may not be classified. Four crystalline modifications[85] are reported for the hexamer, and the transitions recorded here may involve these allotropes. Henderson[62] et al. mentioned two polymeric forms (C and D) with distinct melting ranges. The partial crystillinity of present polymeric sample could account for this fact.

Pseudohalides

Members of the pseudohalides, especially those having the isocyanato-group, have been shown to be energy-rich molecules[126], but experimentally derived energetic data are very scarce. In this work, thermochemical measurements for tricyanophosphine and tri(isocyanato)phosphine via reaction-solution calorimetry are presented (see Chapter six: Thermochemical Results). The synthetic procedures for pseudohalides of phosphorus usually involve exchange reactions, e.g.

$$PCl_3 + 3AgCN = P(CN)_3 + 3AgCl$$

and

$$PCl_3 + 3AgNCO = P(NCO)_3 + 3AgCl$$

An interesting feature of tri(isocyanato)phosphine is its reversible polymerisation. It is reported[114] that a liquid sample of tri(isocyanato)-phosphine (m.pt. = -2 ± 0.5°C, b.pt. = 169.3 ± 0.3°C) remains unchanged upon two weeks standing. However, on supercooling to -20°C, a solid material separates which melts at -2°C. Further, this liquid, on standing for three days, solidifies into a white insoluble material with a m.pt. of ca. 80°C. This solid was distillable to yield the original compound, b.pt. 169.3°C. Another report describes[99] that tri(isocyanato)phosphine "upon standing polymerises to a yellow-white solid". In the present investigation a colourless liquid b.pt. 169°C (lit. 169.3°C) was collected after the completion of the reaction between trichlorophosphine and silver isocyanate. (See Chapter two: Synthesis: for further details). This liquid, on standing for ca. 120 hr. under nitrogen at room temperature, started solidifying into a whitish-yellow material. Two-thirds of the liquid solidified over a period of two months. The solid material (probably polymeric) was distilled to yield a colourless liquid boiling at 40°C/0.5 mm.Hg. Subsequently this liquid was confirmed to be monomeric tri(isocyanato)phosphine, indicating reversible depolymerisation on distillation.

Recently Pollard[99] et al. reported the hydrolysis products of the phosphorus pseudohalides, i.e. tricyanophosphine and tri(isocyanato)phosphine in aqueous sodium hydroxide (5N) and hydrochloric acid (2N). A chromatographic technique was used for the detection of the hydrolysis products. It was found that in hydrochloric acid (2N), phosphorus pseudohalides hydrolyse quantitatively to phosphorus acid and presumably to corresponding hydrogen pseudohalides. In a basic hydrolysing medium, a mixture of lower phosphorus acids with phosphorus acid was obtained. In this investigation samples of tricyanophosphine and tri(isocyanato)phosphine were hydrolysed and the products were quantitatively estimated by a potentiometric technique, e.g.

$$P(CN)_3 + 3H_2O = H_3PO_3 + 3HCN$$

For tricyanophosphine three end-points were detected, corresponding to pk($H-H_2PO_3$) = 1.8, pk($H-HPO_3^-$) = 6.15, and pk(H-CN) = 9.14. The purity of the sample, based on the corresponding titres, indicated a purity of 99.02% for tricyanophosphine. A similar hydrolysis of freshly-distilled tri(isocyanato)-phosphine produced three end-points (see Appendix one: Potentiometric Results) pk($H-H_2PO_3$) = 1.8, pk($H-HPO_3^-$) = 6.15 and pk(H-NCO) = 3.70. On the basis of the corresponding titres for the first and third end-points (i.e. phosphorus acid end points) a purity of 98.33% was found for tri(isocyanato)phosphine. Calculations based on the isocyanic acid end-point gave a purity of ca. 74%. It is known with certainty that isocyanic acid decomposes[227,228] rapidly in acid solution

$$HNCO + H_3O^+ \longrightarrow CO_2 + NH_4^+$$

This fact accounts for the anamolous isocyanic acid end-point.

Owing to the reversible polymerisation of tri(isocyanato)phosphine, it is essential that the molecular weight be known exactly at the time of hydrolysis in the calorimeter. A sample was shown to be monomeric by molecular weight determination (see Appendix two: Cryoscopic Results). This molecular weight determination was performed on a freshly-distilled sample of tri(isocyanato)-phosphine which was stored under dry nitrogen for 12 hr. Due to the hygroscopic nature of this compound all operations were performed under an inert atmosphere of nitrogen. A cryoscopic method was used using naphthalene for calibration and testing with phenyldichlorophosphine. The result for the molecular weight determination of phenyldichlorophosphine is in excellent agreement with calculated.

For both tricyanophosphine and tri(isocyanato)phosphine, the reaction selected for the thermochemical study was the hydrolysis.

$$P(CN)_3(c) + 3H_2O(l) = (H_3PO_3 + 3HCN)(sol.) \quad H_{obs.} = -49.58 \pm 0.12 \text{ kcal mole}^{-1}$$

The enthalpies of reaction were determined via constant-temperature-environment (C.T.E.) calorimetry as the reactions were fast (main period for reaction was less than 2 min.). The $\Delta H_{obs.}$ recorded for tri(isocyanato)-phosphine was -79.81 ± 0.31 kcal mole^{-1}. Using the following ancillary data in the thermodynamic equation above, it can be seen that the standard heat of formation of tricyanophosphine is 133.63 ± 0.4 kcal mole^{-1}. The literature data for ΔH_f^o (H_3PO_3,aq.) = -228.9 ± 0.3 kcal mole^{-1},[229] ΔH_f^o (HCN,aq.) = 36.0 ± 0.1[210] kcal mole^{-1} and ΔH_f^o H_2O,liq. = -68.317[210] kcal mole^{-1}.

A similar evaluation of the standard heat of formation for tri(isocyanato)-phosphine is complicated by the fact that one of the reaction products (i.e. isocyanic acid) decomposes at a significant rate in acid solution. Lister[227] has studied the kinetics of this decomposition under a variety of conditions.

Accordingly, in acid solution at 0°C, the rate constant K_2 is equal to 0.86 mole, l^{-1}, min^{-1} and the activation energy, E_a equals to 14.5 kcal. From these data the half-life of the reaction at 25°C is deduced to be between 3 and 7 min. As this time is comparable with the length of the main period for the hydrolysis (1-2 min.), no accurate derived data can be obtained.

Phosphorus (III) and Phosphorus (V) Compounds

Although numerous compounds of these classes are reported in the literature, energetic data are mainly limited to symmetric derivatives[65] e.g. (PX_3, x = halogen, alkyl, or aryl). The preparation of phenyltetrabromophosphorane and phenyltetrachlorophosphorane is based on the following reactions in carbon tetrachloride.

$$C_6H_5PBr_2 + Br_2 = C_6H_5PBr_4$$

$$C_6H_5PCl_2 + Cl_2 = C_6H_5PCl_4$$

In the present investigation phenyldichlorophosphine has been utilized as a synthetic precursor for the phosphobenzene. Both phenyldibromophosphine and phenyltetrabromophosphorane were degradation products from the thermochemical reaction of phosphobenzene (i.e. $(C_6H_5P)_5$ and $(C_6H_5P)_n$). Hence a knowledge of their thermochemistry is important. The hydrolysis products of phenyldibromophosphine and phenyltetrabromophosphorane were quantitatively evaluated prior to calorimetry (see Chapter six: Thermochemical Results). Hydrolysis was shown to be quantitative according to the following equations.

$$C_6H_5PBr_2 + 2H_2O = C_6H_5PO_2H_2 + 2HBr$$

$$C_6H_5PBr_4 + 3H_2O = C_6H_5PO_3H_2 + 4HBr$$

$$C_6H_5PBr_2 + Br_2 + 3H_2O = C_6H_5PO_3H_2 + 4HBr$$

The thermochemical reaction for phenyltetrabromophosphorane hydrolysis was $C_6H_5PBr_4(\text{cryst.}) + 3H_2O(l) = (C_6H_5PO_3H_2 + 4HBr)(\text{sol.})$ $\Delta H_{obs.} = -80.56 \pm 0.14$ kcal. and the ΔH_f^o for $C_6H_5PBr_4$ can be derived if the relevant ancillary data are available. In the absence of reliable data for phenylphosphonic acid the derivable data are

$$\Delta H_f^o\ (C_6H_5PBr_4,(c))\ -\ \Delta H_f^o\ (C_6H_5PO_3H_2(aq))\ =\ 169.31\ \pm\ 0.5\ \text{kcal mole}^{-1}$$

Similarly

$$C_6H_5PBr_2(l)\ +\ 2H_2O(l)\ =\ (C_6H_5PO_2H_2\ +\ 2HBr)(sol.)\ \Delta H_{obs.}\ =\ -41.7\ \pm\ 0.08\ \text{kcal mole}^{-1}$$

$$\Delta H_f^o\ (C_6H_5PBr_2(l))\ -\ \Delta H_f^o\ (C_6H_5PO_2H_2(aq))\ =\ 120.2\ \pm\ 0.2\ \text{kcal mole}^{-1}$$

Also

$$C_6H_5PBr_2(l)\ +\ Br_2\ aq.\ +\ 3H_2O(l)\ =\ (C_6H_5PO_3H_2\ +\ 4HBr)\ aq.\quad H_{obs.}\ =\ -104.36\ \pm\ 0.13\ \text{kcal mole}^{-1}$$

$$\Delta H_f^o\ (C_6H_5PBr_2(l))\ -\ \Delta H_f^o\ (\ C_6H_5PO_3H_2(aq.))\ =\ 193.7\ \pm\ 0.4\ \text{kcal mole}^{-1}$$

Using ancillary data for ΔH_f^o HBr aq. = -29.05 ± 0.09 kcal mole^{-1} [230], ΔH_f^o H_2O = -68.317[210], ΔH_f^o Br_2 aq. = -0.62 kcal mole^{-1} [210]. Heats of mixing of the products were ignored.

Molecular Adducts

There are numerous complexes[72,148,151,231] of phosphorus (III) and phosphorus (V) compounds with the trihalides of the main group three elements (see Appendix six: Classification: for illustration). A recent publication[148,151,231] and a review[72] reveal the importance of thermochemical measurements for understanding the nature of complexing. The present work is concerned with the thermochemistry of diphosphorus tetraiodideboron tribromide (1:2) adduct and pentabromophosphorane-boron tribromide, and mass-spectrometric studies for tribromophosphine-boron triiodide and triiodophosphine-boron tribromide. Using a thermal analysis technique it was attempted to determine relative bond strengths for each boron tribromide in the diphosphorus tetraiodide-boron tribromide (1:2) adduct. The syntheses of the molecular adducts were carried-out by allowing the two components to react in the presence of dichloromethane and or carbon disulphide. Some syntheses (e.g. $P_2I_4 2BBr_3$) proceed more smoothly in the absence of solvent. The results from the thermochemical investigation for the diphosphorus tetraiodide-boron tribromide (1:2) adduct are presented in the thermodynamic cycle shown on P217 . It can be seen that the enthalpy of complexing ($P_2I_4 2BBr_3$) for the components in their standard states is -2.13 ± 0.29 kcal mole^{-1}. This evaluation assumes that the equilibrium in carbon disulphide is rapidly attained. Constant temperature environment calorimetry was used for step (3) and adiabatic calorimetry for step (1) and (2) (see Chapter three: for calorimetric technique). The standard heat of formation for diphosphorus tetraiodide-boron tribromide (1:2) adduct is derived from

$$P_2I_4 2BBr_3(c) = P_2I_4(c) + 2BBr_3(l), \ \Delta H = +2.13 \pm 0.29 \text{ kcal mole}^{-1}$$

$$\Delta H_f^o \ (P_2I_4 2BBr_3,(c)) = -144.0 \pm 1.6 \text{ kcal mole}^{-1}$$

$$\begin{tikzcd}
P_2I_4 2BBr_3\,(\text{sol.}) \arrow[r, phantom, "\rightleftharpoons"] & & P_2I_4(\text{sol.}) + 2BBr_3(\text{sol.}) \\
P_2I_4 2BBr_3\,(\text{cryst.}) \arrow[u, "(1)"] & (\text{in } CS_2) & \\
P_2I_4(\text{cryst.}) + 2BBr_3(\text{liq.}) \arrow[u, "(4)"] & & P_2I_4(\text{cryst.}) + 2BBr_3(\text{sol.}) \arrow[ll, "(3)"'] \arrow[uu, "(2)"']
\end{tikzcd}$$

Kcal (x4·184=KJ)

$$\Delta H_{(1)} = -26\cdot75 \pm 0\cdot27$$

$$\Delta H_{(2)} = -28\cdot34 \pm 0\cdot11$$

$$\Delta H_{(3)} = 0\cdot54 \pm 0\cdot001$$

$$\therefore \Delta H_{(4)} = \Delta H_{(3)} + \Delta H_{(2)} - \Delta H_{(1)}$$

$$\Delta H_{(4)} = -2\cdot13 \pm 0\cdot29 \text{ Kcal mole}^{-1}$$

Fig. Thermodynamic cycle for diphosphorus tetraiodide-boron tribromide (1:2) adduct.

using the literature ancillary data for

ΔH_f^o (P_2I_4(c)) = -27.03 ± 1.19 kcal mole^{-1} [104]

ΔH_f^o (BBr_3,(l)) = -57.4 ± 0.5 kcal mole^{-1} [230]

Since the (1:1) molecular adduct of diphosphorus tetraiodide with boron tribromide is not known, it would be of interest to examine the relative bond strengths for the boron tribromide groups. This has been attempted here via a thermal analysis technique. The results obtained by differential thermal analysis (as shown in Chapter seven) indicate two endotherms over the temperature ranges 82-110°C and 110-131°C, with the corresponding areas of the peaks being 0.50 sq.in. and 0.66 sq.in. It is probable that the first endotherm corresponds to the loss of two molecules of boron tribromide (normal b.pt. of boron tribromide is 91°C). It is equally likely that the second endotherm corresponds to the melting of diphosphorus tetraiodide (m.pt. P_2I_4 = 124.5°C). Hence the 1:1 adduct cannot be detected by thermal analysis.

The complex pentabromophosphorane-boron tribromide (probably $PBr_4^+ BBr_4^-$) was studied thermochemically via its hydrolysis in a CTE calorimeter

PBr_5BBr_3(c)+7H_2O(l) = (H_3PO_4+H_3BO_3+8HBr)sol., $\Delta H_{obs.}$ = -179.06±0.26 kcal mole^{-1}

ΔH_f^o (PBr_5BBr_3(c)) = -142.0 ± 1.3 kcal mole^{-1}

The ancillary data are: ΔH_f^o (H_2O(l)) = -68.317 ± 0.1 kcal mole^{-1} [210] ΔH_f^o (H_3PO_4(aq.)) = -310.5 ± 1.0 kcal mole^{-1} [37,210] ΔH_f^o (H_3BO_3(aq.)) = -256.35 ± 0.2 kcal mole^{-1} [230] ΔH_f^o (HBr,(aq.)) =-29.05 ± 0.09 kcal mole^{-1} [230].

SECTION-V. APPENDIX

CHAPTER ELEVEN: POTENTIOMETRIC TITRATION RESULTS

CRYOSCOPIC RESULTS

VIBRATIONAL SPECTROSCOPIC RESULTS

X-RAY ANALYSIS RESULTS

APPENDIX ONE

Potentiometric Titration Results

This appendix contains the potentiometric titration graphs for the analyses of tricyanophosphine and tri(isocyanato)phosphine.

Two graphs are presented for each compound (i) pH Vs V and (ii) $\Delta pH/\Delta V$ Vs $\overline{V}$. For tricyanophosphine, hydrolysis proceeded according to

$$P(CN)_3 + 3H_2O = H_3PO_3 + 3HCN$$

Three end-points were detected corresponding to $pK(H\text{-}H_2PO_3) = 1.8$[160], $pK(H\text{-}HPO_3) = 6.15$[160] and $pK(H\text{-}CN) = 9.14$[161].

For tri(isocyanato)phosphine, hydrolysis proceeded according to

$$P(NCO)_3 + 3H_2O = 3HNCO + H_3PO_3$$

Three end-points were detected, corresponding to $pK(H\text{-}H_2PO_3) = 1.8$[160], $pK(H\text{-}HPO_3) = 6.15$[160], and $pK(H\text{-}NCO) = 3.70$[161].

For tricyanophosphine, the titres indicate a purity of 99.0%.

For tri(isocyanato)phosphine, the first and third end-points (these for H_3PO_3) indicate a purity of 98.3%. The end-point for isocyanic acid gives anomalous results due to the decomposition of HNCO in acid solution (see Chapter ten: Discussion).

Details of the experimental equipment used are given in Chapter two.

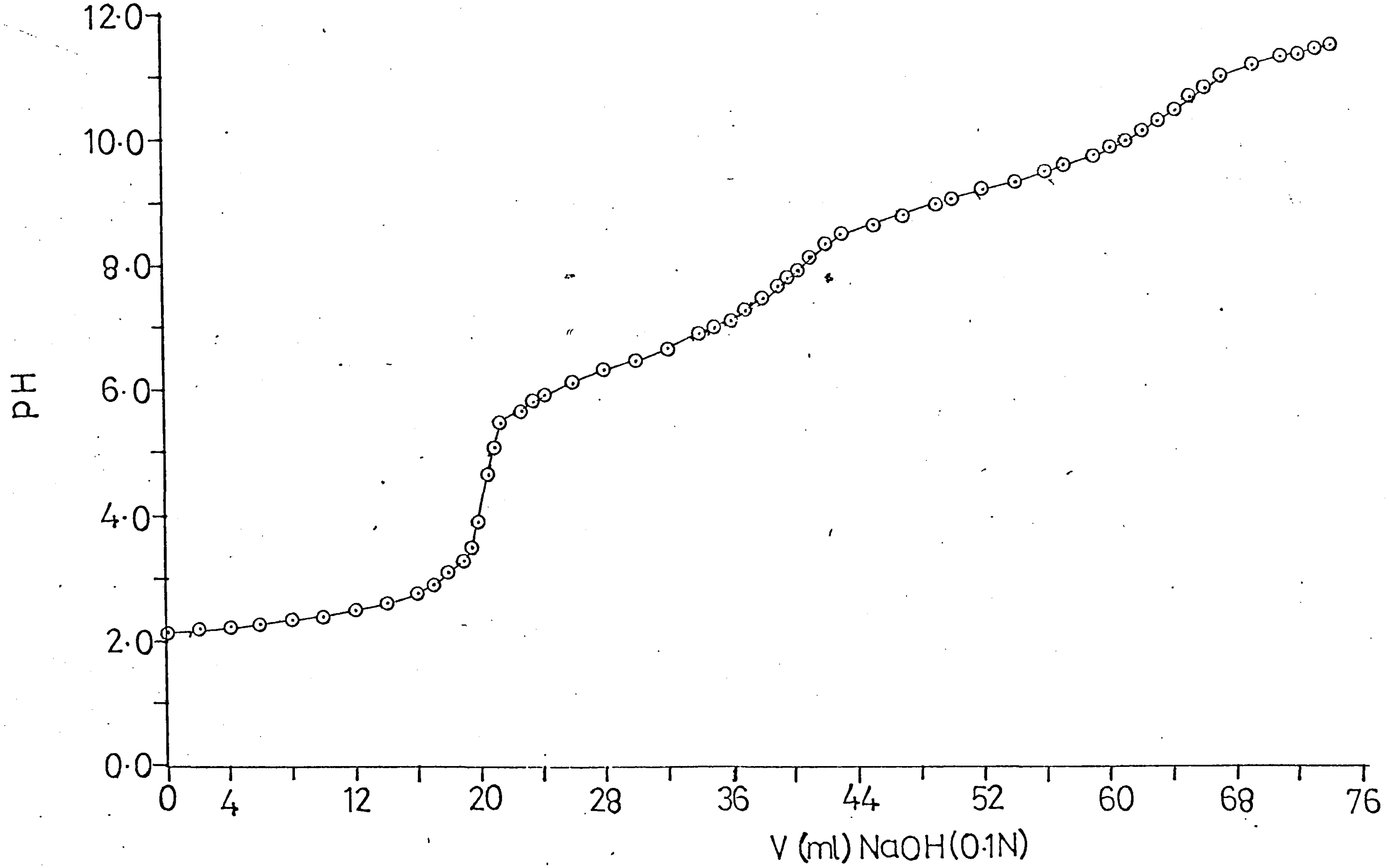
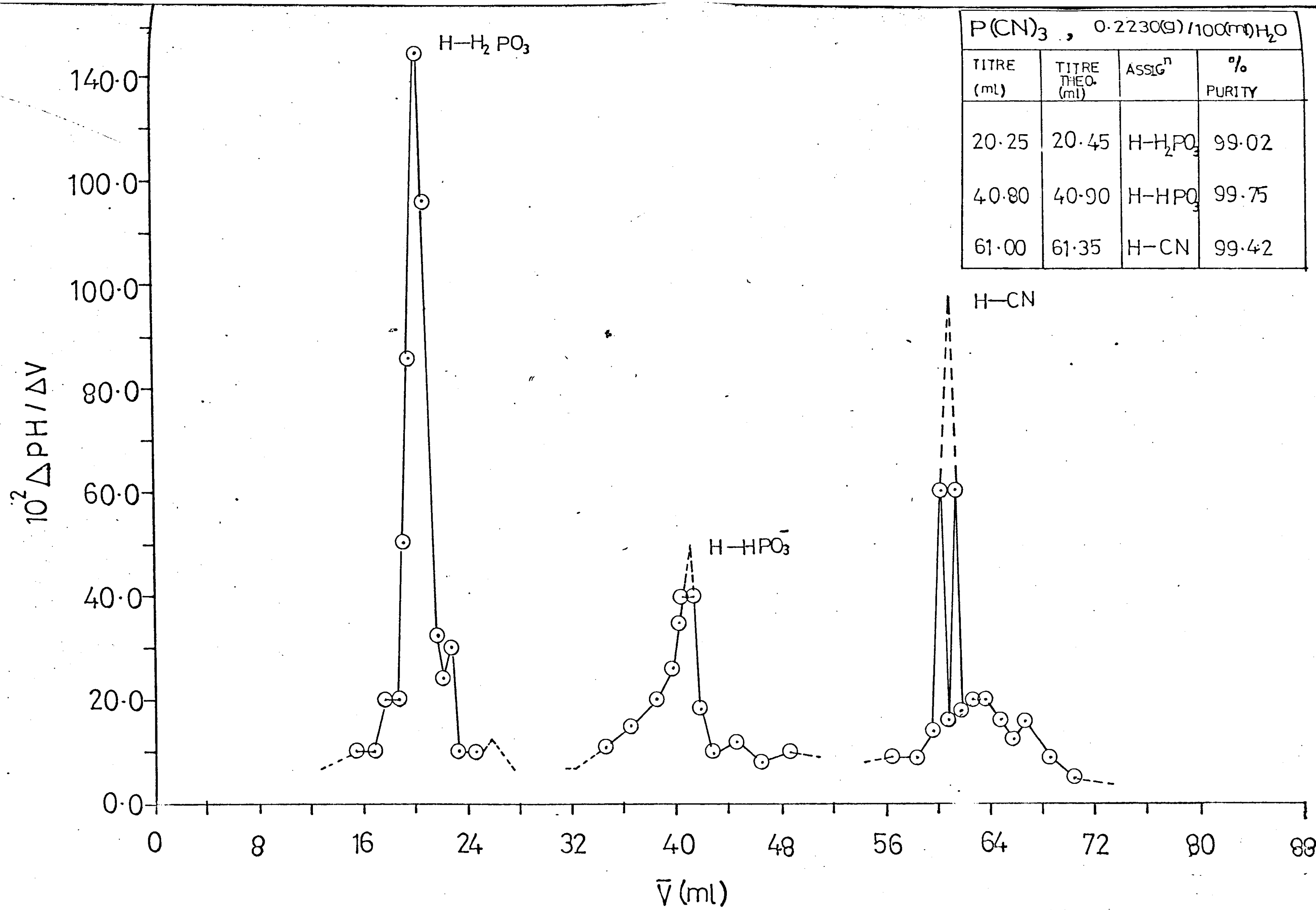


Fig. Potentiometric Titration Graph of the Hydrolysate of Tricyanophosphine.



P(CN)$_3$, 0·2230(g)/100(ml)H$_2$O

TITRE (ml)	TITRE THEO. (ml)	ASSIG^n	% PURITY
20·25	20·45	H-H$_2$PO$_3$	99·02
40·80	40·90	H-HPO$_3$	99·75
61·00	61·35	H-CN	99·42

Fig. Derivative Graph for the Potentiometric Titration of Tricyanophosphine.

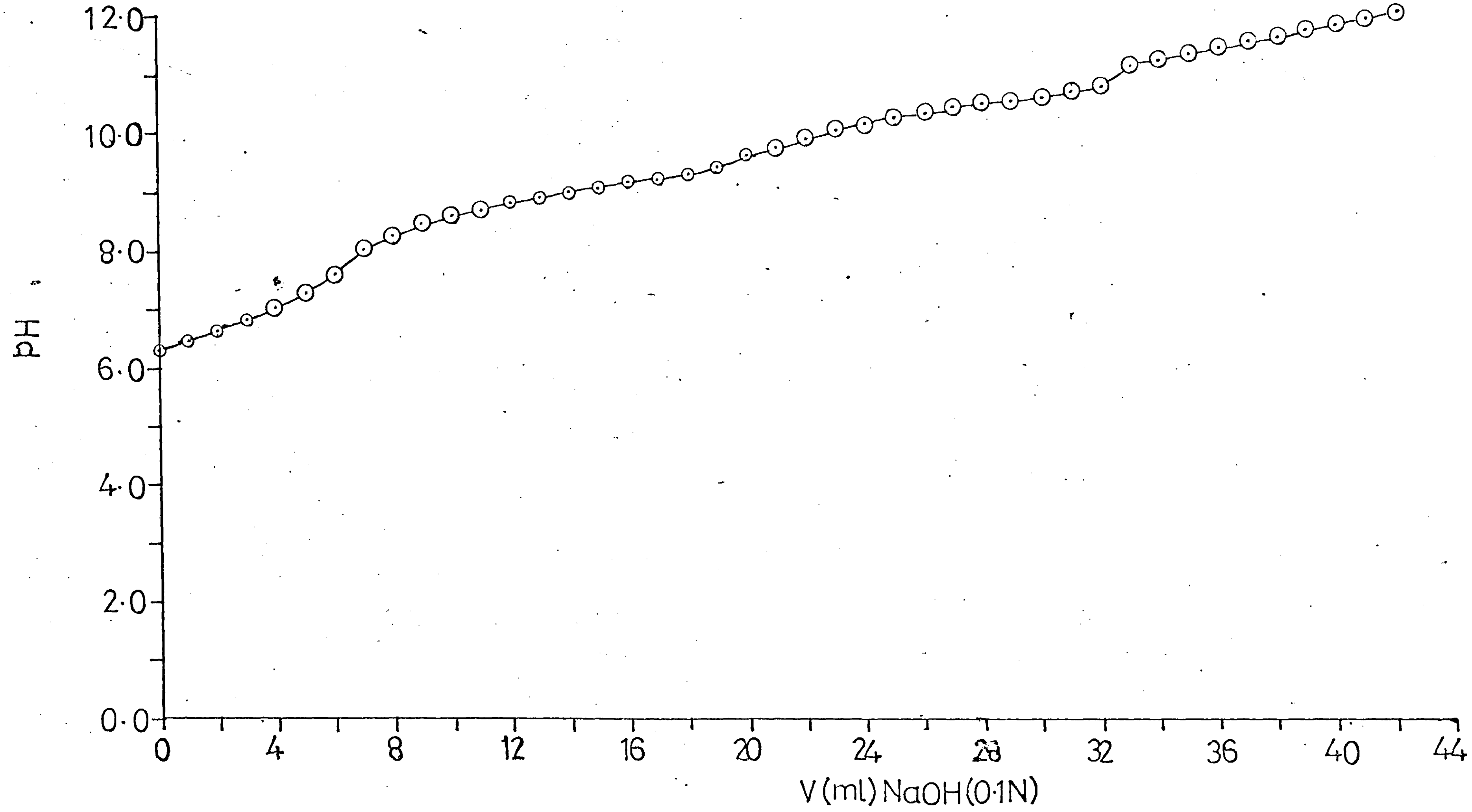
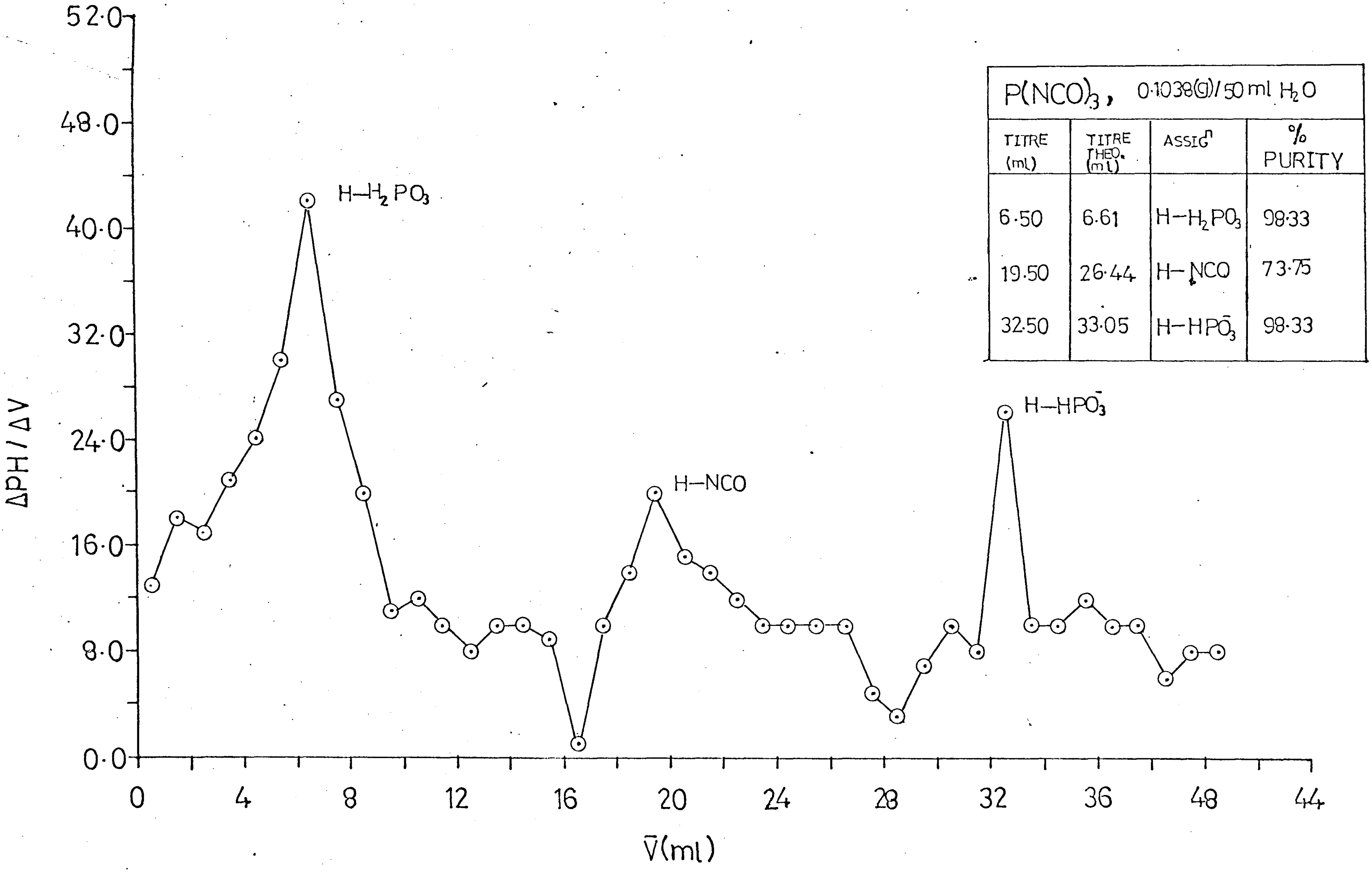


Fig. Potentiometric Titration Graph of the Hydrolysate of Tri(isocyanato)phosphine.



$P(NCO)_3$, 0·1038(g)/50 ml H_2O			
TITRE (ml)	TITRE THEO. (ml)	ASSIGⁿ	% PURITY
6·50	6·61	H—H_2PO_3	98·33
19·50	26·44	H—NCO	73·75
32·50	33·05	H—HPO_3^-	98·33

Fig. Derivative Graph for the Potentiometric Titration of Tri(isocyanato)phosphine .

APPENDIX TWO

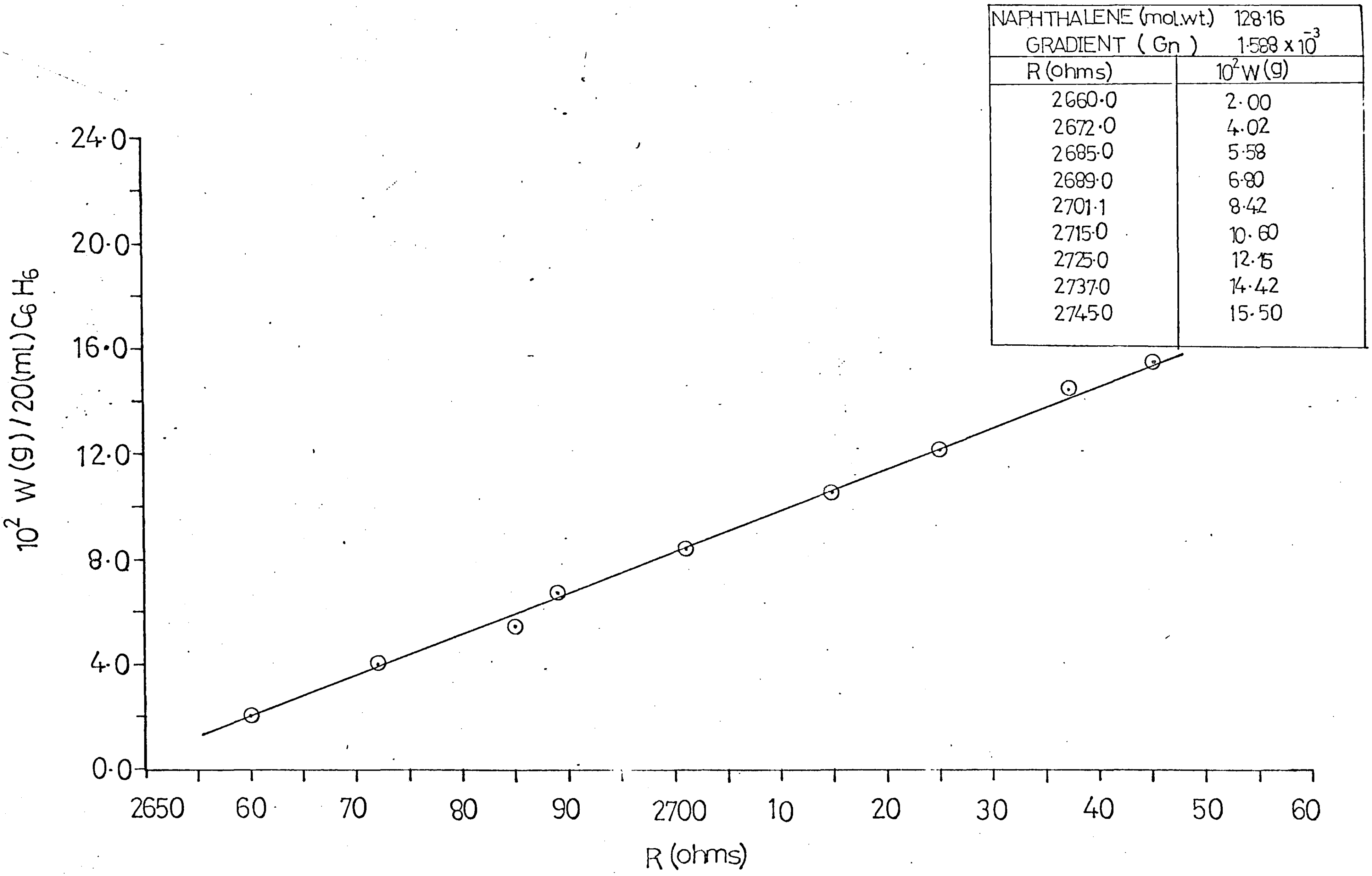
Cryoscopic Results

This appendix contains detailed results of molecular weight determinations via cryoscopy. Details of the apparatus and method are on p. 66 The results are presented in the form of graphs of weight of dissolved solute per 20 ml. benzene (solvent) vs. the freezing point (in Ω). The graphs are given in the following order.

(i) Naphthalene (calibration) Mol. wt. (calc.), 128.16.

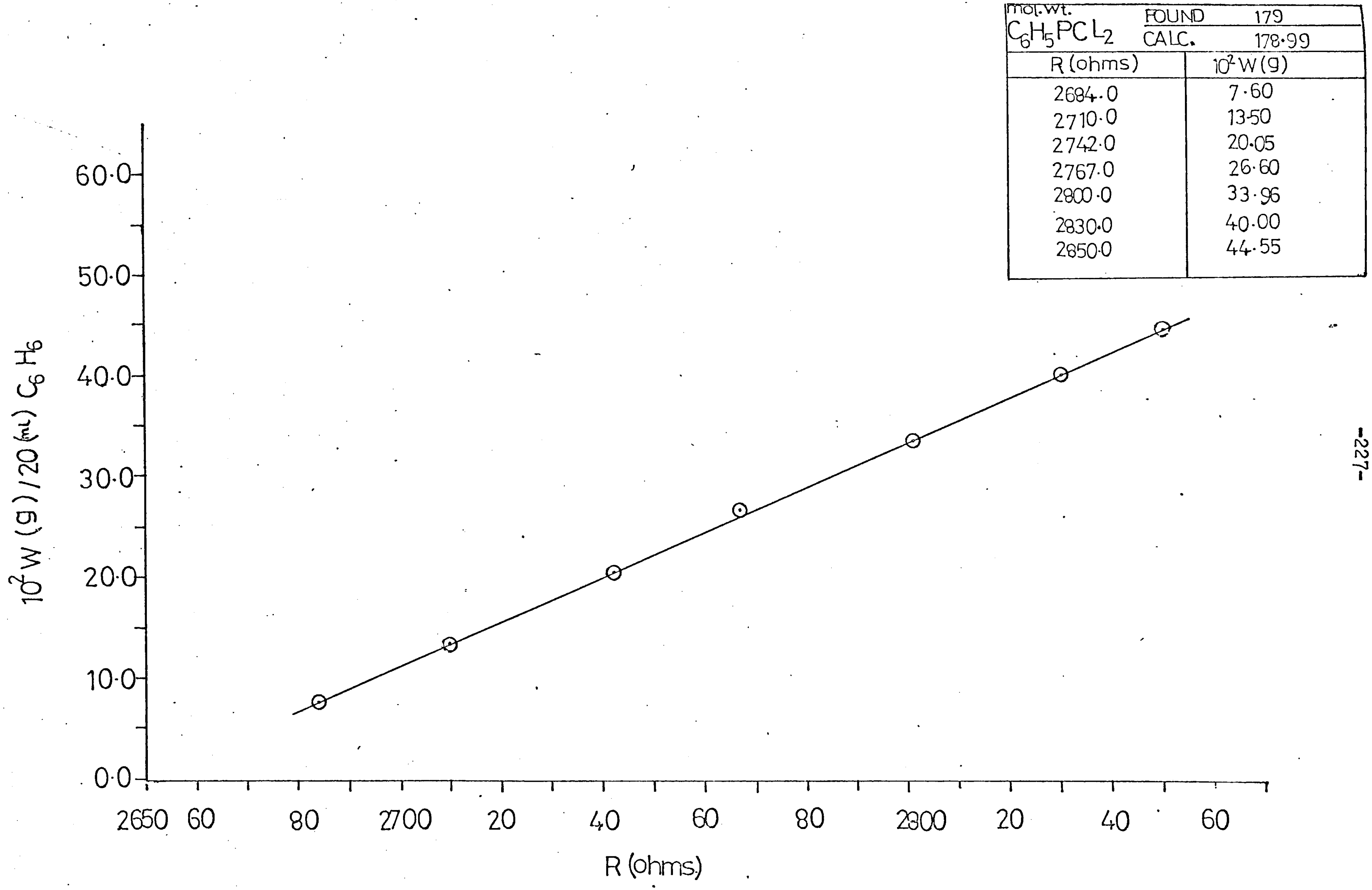
(ii) $C_6H_5PCl_2$ (Test compound) Mol. wt. (calc.), 178.99; Found, 179.

(iii) $P(NCO)_3$, distilled and stored at ambient under nitrogen for 11.5 hr.
Mol. wt. (calc.), 157.02; Found, 161.



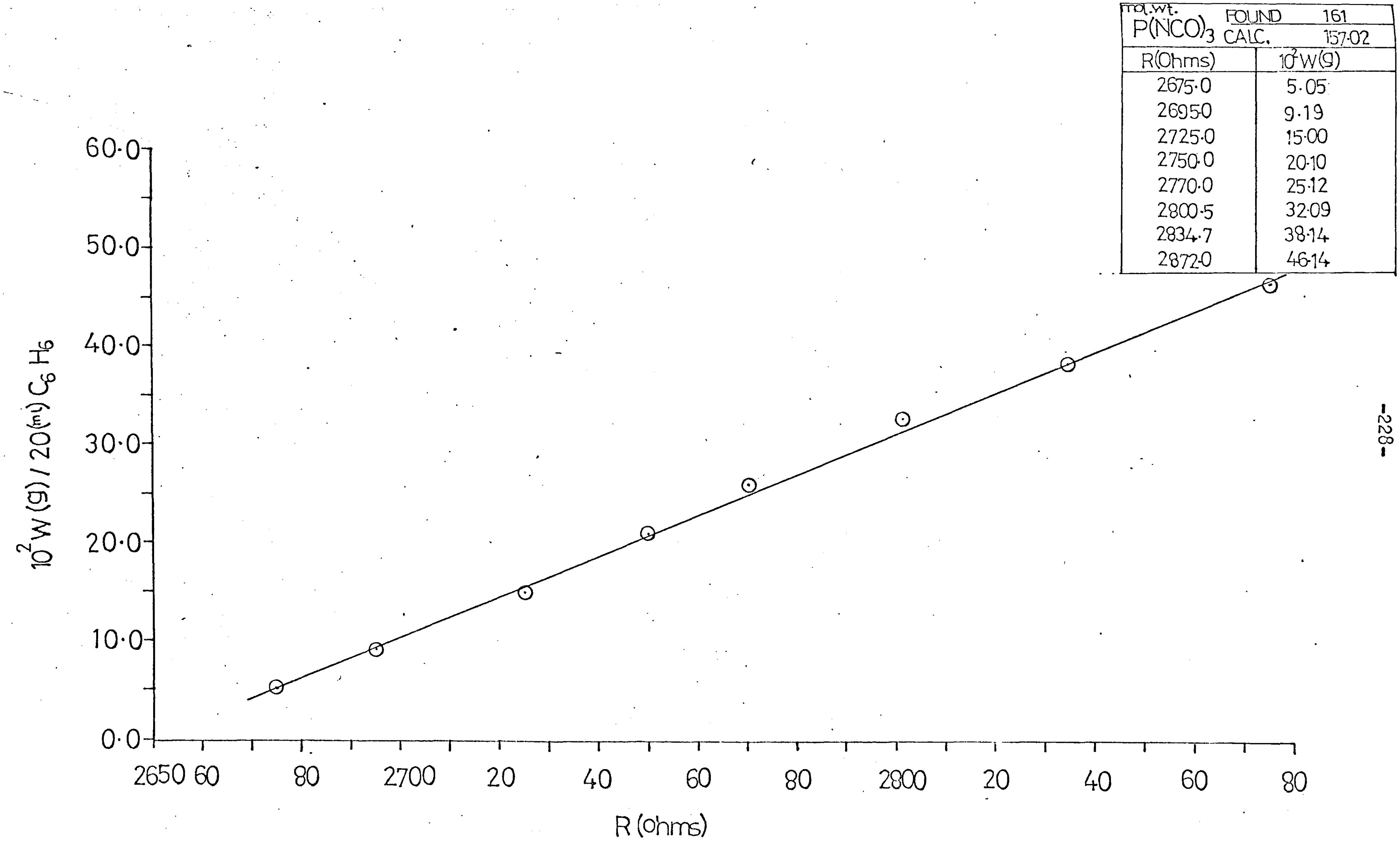
NAPHTHALENE (mol.wt.)	128·16
GRADIENT (Gn)	$1{\cdot}588 \times 10^{-3}$
R (ohms)	10^2W(g)
2660·0	2·00
2672·0	4·02
2685·0	5·58
2689·0	6·80
2701·1	8·42
2715·0	10·60
2725·0	12·15
2737·0	14·42
2745·0	15·50

Fig. Concentration of Naphthalene in Benzene vs. Freezing Point (in ohm.) of Solution.



mol.wt. $C_6H_5PCL_2$	FOUND 179 CALC. 178·99
R (ohms)	10^2 W (g)
2684·0	7·60
2710·0	13·50
2742·0	20·05
2767·0	26·60
2800·0	33·96
2830·0	40·00
2850·0	44·55

Fig. Concentration of Phenyldichlorophosphine in Benzene vs. Freezing Point (in Chm.) of lution.



mol.wt. $P(NCO)_3$ FOUND 161

CALC. 157·02

R(Ohms)	$10^2 W(g)$
2675·0	5·05
2695·0	9·19
2725·0	15·00
2750·0	20·10
2770·0	25·12
2800·5	32·09
2834·7	38·14
2872·0	46·14

Fig. Concentration of Tri(isocyanato)phosphine in Benzene vs. Freezing Point (in ohm.) of Solution.

APPENDIX THREE

TABLE - Comparison of Raman Spectra

R.L. AMSTER, W.A. HENDERSON and N.B. COLTHUP[172]					THIS WORK	
$(C_6H_5)_4P_4$ (A)		$(C_6H_5)_4P_4$ (B)			$(C_6H_5P)_5$	
$\bar{V}$ (cm^{-1})	RELATIVE INTENSITY	$\bar{V}$ (cm^{-1})	RELATIVE INTENSITY	ASSIGNMENT	$\bar{V}$ (cm^{-1})	RELATIVE INTENSITY
-		3192	0.5			
-		3141	0.5			
3047	1	3052	1	C-H stretch		
-		1581	9	C-C stretch (K,1)	1581	8.2
1578	8	-			-	
-		-			1482	0.6
-		1480	1	C-C stretch (m)	-	
1479	1	-			-	
-		1436	0.5	C-C stretch (n)	-	
					1434	0.4
1431	0.5	-			-	
-		1380	0.5		-	
		1330	0.5	C-C stretch (o)	1330	0.3
1316	0.5	-			-	
-		-			1270	0.5
		1266	0.5	C-H in-plane bend (e)		
1261	0.5	-			-	
					1193	0.8
1190	1	-		C-H in-plane bend (a)	-	
-		1184	1		-	

-		1160	1	C-H in-plane bend (c)	-	
1158	1	-			1158	1.9
-		1095	5	X-sensitive (g)	-	
					1088	4.7
1087	5	-			-	
-		1081	5	C-H in-plane bend (d)	-	
1073	shoulder	-			-	
-		-			1072	2.4
-		1027	5	C-H in-plane bend (b)	-	
					1025	2.0
1024	5	-			-	
-		1001	10	Ring (p)	-	
997	10	-			997	9.5
-		988	shoulder	C-H out-of-plane bend (f)	-	
-		965	0.5	C-H out-of-plane bend (h)		
946	0.5	-			-	
-		936	0.5		-	
925	0.5	-		C-H out-of-plane bend (i)	-	
-		915	0.5		-	
-		-			908	0.7
905	0.5	-			-	
-		867	0.5	C-H out-of-plane bend (g)		
-		-			840	0.5
-		-			744	
-		745	1	C-H out-of-plane bend (f)	-	0.1
736	1	-			-	
-		693	1	X-sensitive (v)	-	
687	1	-			-	

-		-			684	1.0
-		620	1	C-C-C bend(s)	-	
618	1	-			618	2.0
-		-			514	1.4
-		512	shoulder		-	
510	1	-			-	
-		501	6	Asymmetric P-P stretch	-	
-		-			493	2.8
488	3	-			-	
-		-			450	10.0
444	6	-		Symmetric P-P stretch + t + y phenyl vibrations	-	
-		440	6		-	
					428	5.7
-		427	5		-	
422	2	-			-	
-		-			401	2.3
-		398	2		-	
396	1	-			-	
-		-			394	2.4
-		-			374	4.0
370	1	-		P_4 ring + C-P-P deformations + substituent sensitive phenyl vibrations	-	
-		366	0.5		-	
-		329	0.5		-	
-		-			306	0.9
304	1	-			-	
-		289	1		-	
-		-			280	3.5

277	1	-			-	
-		-			263	1.3
-		253	0.5		-	
-		-			236	3.0
-		-			222	1.4
-		219	4		-	
215	1	-			-	
-		-			210	1.9
-		197	1		-	
178	1	-			178	1.8
-		-			155	2.5

TABLE - Comparison of Infra-red Spectra

KUCHEN AND BUCHWAL[84]		THIS WORK			
$(C_6H_5P)_4$		$(C_6H_5P)_5$			
Range: 4000-667 cm^{-1}		Range: 3070-394 cm^{-1}			
$\bar{V}$ (cm^{-1})	Relative Intensity	In KBr disc.		In CS_2 solution	
		$\bar{V}$ (cm^{-1})	Relative Intensity	$\bar{V}$ (cm^{-1})	Relative Intensity
				3070	m
3050	m			3050	m
		1970			
		1952			
		1889			
		1873	w		
		1810			
		1746			
		1647			
		1619			
-		1581	vs		
1580	w	-			
-		1570	vs		
-		1482	vs		
1475	m	-			
-		1435	vs		

1425	m	-			
-		1405	w		
-		1328	m		
1320	w	1320	m		
-		1300	m		
1295	w sh	-			
		1271	w		
		1191	ms		
-		1185	sh		
1180	w	-			
-		1160	m		
1150	w sh	-			
-		1090	ms		
-		1083	sh		
1080	w sh	-			
-		1071	vs		
				1068	m
1050	m	-			
-		1027	vs	1027	s
1020	m				
-		1015	vw		
-		1001	vs		
997	m	-			
-		988	w		
-		980	w		
-		968	w		
900	w	908	s		

-		848	w		
841	w	841	m		
-		833	m		
-		746	w sh		
740	vs	740	ws		
-				737	ws
-		733	ws		
-		692	ws		
-				690	ws
		685	sh		
680	s				
		618	w		
		514	w		
		496	s		
		486	s		
		475	s		
		463	m		
		449	s		
		427	m		
		416	s		
		405	sh		
		400	m		
		394	m		

Legend: s = strong, m = medium, w = weak, sh = shoulder,

v = very

Instrument: IR. s.p. 100, B.W.S: 3, slit: 11, gain: 8.2,

damp: 8.8

APPENDIX FOUR

TABLE - Comparison of X-ray crystallographic results for pentaphenylcyclopentaphosphine

Pentaphenylcyclopentaphosphine		
J. J. DALY[78]	This Work	
Interplanar Spacing $d^*(^\circ A)$	Interplanar Spacing $d(^\circ A)$	Intensity I
13.73	13.80	s
9.18	9.47	s
8.15	8.15	m
6.89	6.88	m
6.80		
	6.19	vwd
5.57	5.59	m
4.87	4.90	md
4.78		
4.59	4.61	m
4.44	4.46	w
4.33	4.34	sd
4.18	4.20	vw
4.03		
3.97	3.96	w
	3.85	m
3.70	3.76	w
3.64	3.67	s

3.52		
3.42	3.45	wd
3.33	3.36	w

Legend: I = Intensity estimated visually

s = strong, m = medium, w = weak, v = very,

d = diffuse

Camara: Phillips-Straumanis, Diameter: 11.46 mm.

Radiation: CuK_{α} , operating condition: 36 Kv, 25 mA.

*These spacings were synthesised by Miss R. S. Osborn (ICULIRS) using a computor programme from Daly's single crystal reflections.

TABLE - Comparison of X-ray crystallographic results for polymeric phenylphosphine$^{(+)}$

Polymeric Phenylphosphine			
L. MAIER (Form D)		THIS WORK	
Interplanar Spacing d(^{o}A)	Intensity	Interplanar Spacing d*(^{o}A)	Intensity I
8.79	vsd	8.66	s
7.51	s	7.57	md
5.31	s	5.26	m
4.50	vsd	4.50	s
		4.38	s
4.03	w	4.01	vw
		3.91	vw
		3.84	vw
3.74	s	3.76	vw
3.50	m	3.49	w
		3.40	w
3.23	s	3.27	m
3.11	w	3.10	vw
3.03	m	3.02	w
2.92	m	2.90	w
2.76	m	2.75	w
2.64	m	2.63	w
		2.56	w
2.52	m	2.53	vw

2.46	vw	2.45	w
2.41	sd	2.41	m

Legend: I = Intensity estimated visually

s = strong, m = medium, w = weak,

v = very, d = diffuse

Camara: Phillips-Straumanis, Diameter: 11.46 mm.,

Radiation: CuK_{α}, operating condition: 36 Kv, 25 mA.

[*] These spacings were synthesised by Miss R. S. Osborn (ICULIRS)

(+) This was prepared by disproportionation of $C_6H_5PF_2$ (see p.48 under synthesis).

APPENDIX FIVE

Of the phosphorus sub-halides (P_2X_4), only P_2Br_4 has not yet been synthesised[65,232] nor characterised energetically.

Kcal $mole^{-1}$

P_2F_4, m.pt. = $-86.5 \pm 0.5^{\circ}C$,[221] $\Delta H^{o}f\ (P_2F_4(g)) = -290$[25]

P_2Cl_4, m.pt. = $-34^{\circ}C$,[65,232,233] $\Delta H^{o}f\ (P_2Cl_4(l)) = -106$[74]

P_2I_4, m.pt. = $124.5^{\circ}C$,[157] $\Delta H^{o}f\ (P_2I_4(c)) = -27$[104]

It is interesting to estimate the standard heat of formation of diphosphorus tetrabromide using the following expressions.

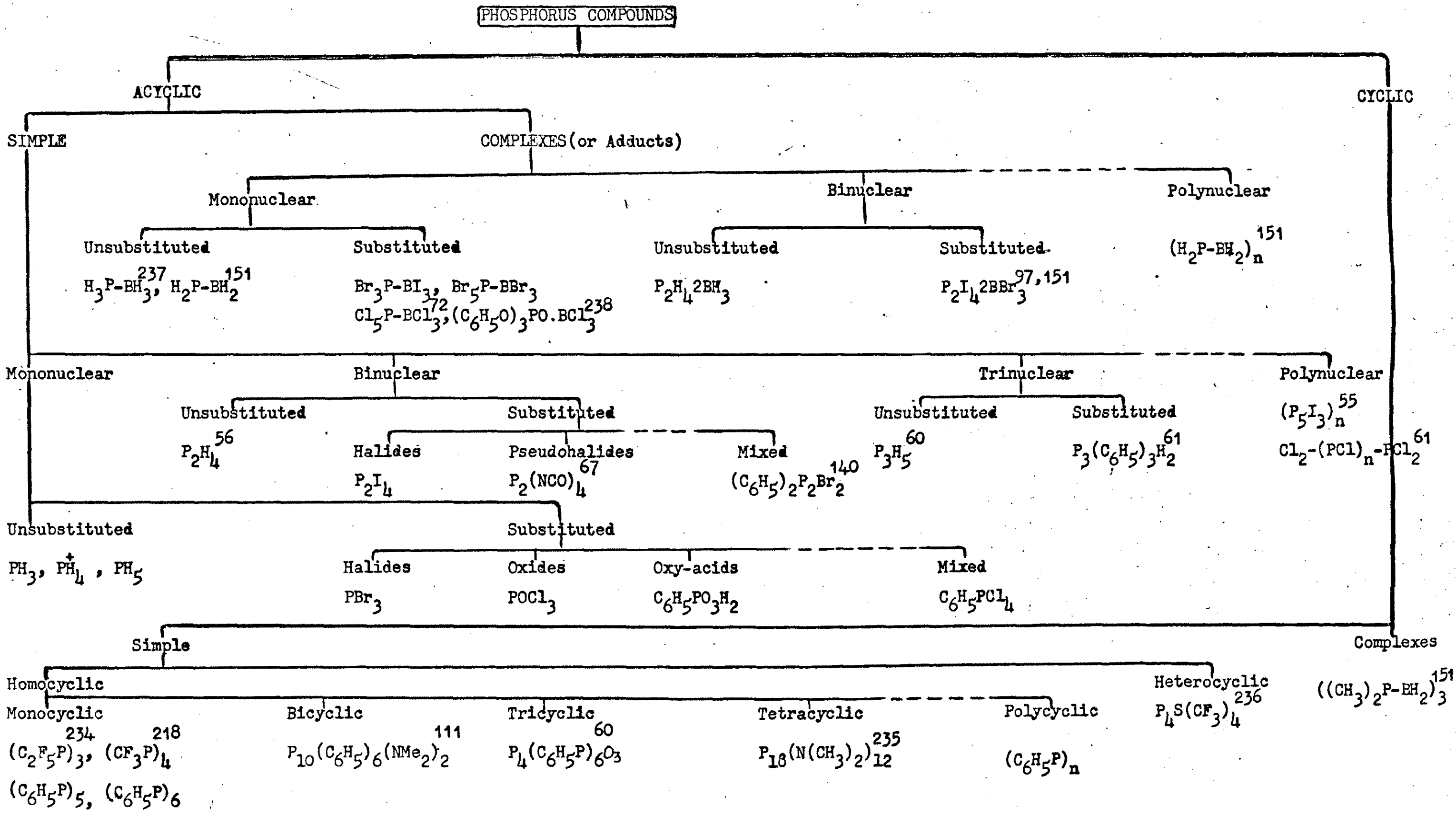
$$E_{P-P} + 4E(P - Br) = 2\ \Delta H^{o}f(P,(g)) + 4\ \Delta H^{o}f(Br,(g)) - \Delta H^{o}f(P_2Br_4(c)) - \Delta H(P_2Br_4(c \rightarrow g))$$

Taking $E_{(P-P)}$ as in diphosphorus tetraiodide[76] and E(P-Br) as in tribromophosphine[25] (i.e. 62 and 64 kcal respectively, $\Delta H^{o}f(P,(g))$ 75.5 kcal, $\Delta H^{o}f(Br,(g)) = 27$ kcal and estimating $H(P_2Br_4(c \rightarrow g)) = 10 \pm 5$ kcal $mole^{-1}$ we have

$$\Delta H^{o}f\ (P_2Br_4(c)) \simeq -69 \pm 5 \text{ kcal mole}^{-1}$$

APPENDIX SIX

CLASSIFICATION :



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THE PHOSPHORUS-PHOSPHORUS BOND ENERGY IN DIPHOSPHORUS TETRA-IODIDE

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Abstract—The enthalpies of sublimation at 298·15 K of phosphorus tri-iodide and diphosphorus tetra-iodide (15·2±0·9 and 16·7±0·5 kcal. mole^{-1} respectively) have been determined using an effusion manometer. Combination of these enthalpies with literature thermodynamic data gives an estimate of 62 kcal for the phosphorus-phosphorus bond energy in P_2I_4.

INTRODUCTION

THERE is considerable current interest in compounds containing the phosphorus-phosphorus bond[1]. A feature of such compounds is the nearly constant phosphorus-phosphorus bond length (2·21 Å), a possible exception being the sulphide, P_4S_7. In contrast, estimates of the phosphorus-phosphorus bond energy, E(P—P), or of the bond dissociation energy, D(P—P), are divergent (*vide infra*). The former derive from thermochemical investigations while the latter stem from appearance potential data obtained from electron-impact studies.

Recently, the standard enthalpy of formation of P_2I_4 has been reported[2] in conjunction with a revised corresponding figure for PI_3. Combination of these data with the enthalpies of sublimation for these iodides, the determination of which is described in this paper, yields E(P—P) in P_2I_4. The sublimation enthalpy is always the most difficultly accessible function for the determination of bond energies in compounds whose standard state are crystalline and which melt with decomposition.

EXPERIMENTAL

The manometer

An effusion manometer was constructed to a design similar to that of Kington and Edwards[3]. In view of the corrosive nature of the phosphorus iodides the effusion cell was fabricated in stainless steel (B) and the foil (C) in gold. (Fig. 1b). The foil was retained in position by a stainless-steel locking ring. Kington and Edwards used a film of Apiezon N lubricant on the walls and the base of the cell to ensure good contact between the cell and block. This film must be quantitatively removed prior to weighing at the end of each run. This has proved difficult[4] and hence the cell in this apparatus was screwed into the block via a precision thread (26 t.p.i., Whitworth) (see Fig. 1). The foil was drilled using a No. 80 high speed twist drill, and burrs removed with a fine abrasive paste. The radius was determined by photomicrography (linear magnification × 100) followed by planimetry. The thickness was deduced from a knowledge of the weight, density and surface area of the foil. A mercury diffusion pump backed by a two-stage rotary pump gave a pressure of 10^{-5} mm of Hg at the mano-

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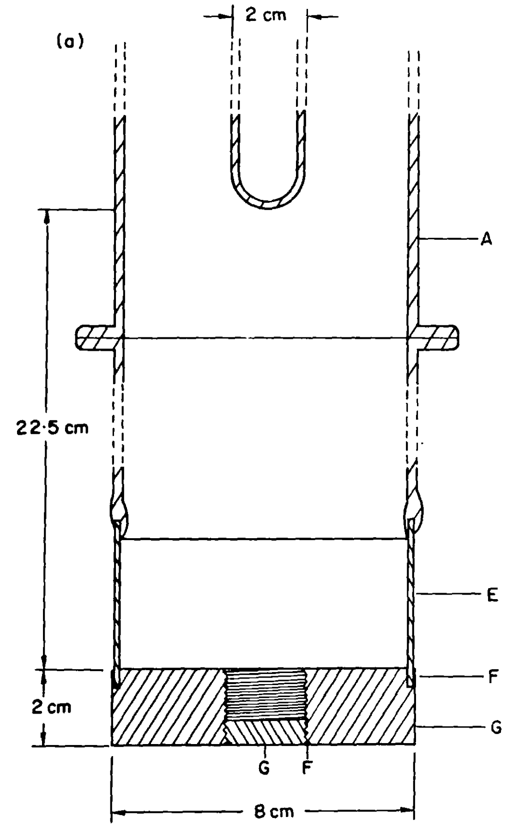

Fig. 1(a). Section through block and cold-finger. A, Pyrex glass; E, Kovar metal; F, Silver solder; G, Copper.

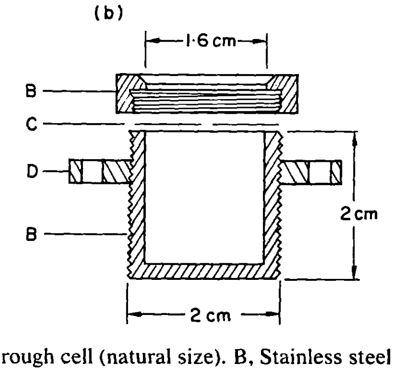

Fig. 1(b). Section through cell (natural size). B, Stainless steel; C, Gold foil; D, Duralumin yoke.

meter. Individual runs were *ca.* 24 hr in duration and condensation was achieved using an acetone/solid CO_2 mixture. The temperatures were determined as follows: (i) over the range 21–27°C, a mercury-in-glass thermometer reading to ±0·002°C and calibrated against a Quartz Crystal Thermometer (Hewlett–Packard) was used, and (ii) over the range 54–80°C, an NPL-calibrated mercury-in-glass thermometer accurate to ±0·02°C was used. For the lower temperature range the block was thermostatted to ±0·001°C in a water bath, and over the higher range, to ±0·02°C in an oil bath.

RESULTS

Testing the manometer

There are two independent reliable determinations of the vapour pressure of ferrocene over the range 20–28°C via effusion manometry[3, 5]. Kington and Edwards (KE), who review the earlier work, obtain systematically higher vapour pressures than Andrews and Westrum (AW) but the enthalpies of sublimation are concordant. The ferrocene (BDH) used in this work was twice crystallised from absolute ethanol and sublimed *in vacuo*, m.p. 175–176°C, lit.[6] m.p. 175·5–176°C. This is a modification of the purification procedure of Edwards *et al.*[6].

The equation to convert material loss from the cell to equilibrium vapour pressure is

$$p = \frac{w}{tA}\left[\frac{2\pi RT}{M}\right]^{1/2}\left[\frac{8r+3l}{8r}\right]\left[\frac{1}{1+0{\cdot}48\,r/2\lambda}\right]$$

where $p =$ pressure (dynes cm^{-2}), $\lambda =$ mean free path ($= kT/\sqrt{2}\pi\sigma^2 p$) (cm), $r =$ radius of effusion orifice (cm), $l =$ length of orifice (cm), $R =$ gas constant (ergs. deg^{-1} mole^{-1}), $M =$ molecular wt., $T =$ absolute temp. (K), $w =$ weight loss (g), $t =$ time (sec) and $A =$ orifice area (cm^2). The second term in brackets corrects the ideal Langmuir expression for finite orifice length, and the third term takes account of the fact that the ratio of the mean free path to orifice diameter is significant (in this work, $5 < \lambda/d < 20$). This expression is fully discussed by Kington and Edwards[3] and Carman[7].

Table 1

	$\Delta H(c \rightarrow g)298$ (kcal. mole^{-1})	$p\,298$ (mm of Hg)
KE	17·53 ± 0·10	0·00684
AW	17·38 ± 0·13	0·00714
This work	17·84 ± 0·96	0·00680

The results were obtained by a least squares analysis and the uncertainty interval was $\pm[\sum_i r_i^2/(n-2)(\sum_i x_i^2 - n\bar{x}^2)]^{1/2}$ where $r =$ residual, $x = T^{-1}$ and $n =$ no. of sets. Also, throughout this paper 1 cal = 4·1840 Joule, 1 mm Hg = 0·133322 kNm^{-2} and 1 Å = 0·1 nm.

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Vapour pressures of the phosphorus iodides

Orifice area (A) = $1{\cdot}074\times10^{-3}$ cm^2 ($r = 1{\cdot}849\times10^{-2}$ cm) Orifice length (l) = $2{\cdot}670\times10^{-3}$ cm.

Table 2. Phosphorus tri-iodide

T (°K)	$10^7 w/t$ (g. sec^{-1})	$10^3 p$ (mm of Hg)
294·137	1·8750	2·634
294·137	1·8750	2·634
295·134$_5$	1·9861	2·793
295·134$_5$	2·1111	2·966
296·132	2·3055	3·241
296·132	2·3055	3·241
297·134	2·3750	3·343
297·134	2·4166	3·400
298·136	2·6944	3·791
298·136	2·8611	4·021
299·136	2·8333	3·989
300·137	3·1250	4·399

Experiments with P_2I_4 over a range including 25°C yielded irreproducibly small material loss.

Table 3. Diphosphorus tetra-iodide

T (°K)	$10^7 w/t$ (g. sec^{-1})	$10^3 p$ (mm of Hg)
328·09	1·3079	1·661
328·09	1·2847	1·632
328·09	1·2731	1·617
330·09	1·4930	1·899
331·09	1·4930	1·902
333·08	1·7361	2·215
333·08	1·7130	2·186
333·08	1·7245	2·200
333·08	1·7130	2·186
338·06	2·6157	3·341
338·06	2·5926	3·312
343·04	3·6805	4·702
343·04	3·5069	4·485
343·04	3·5185	4·500
343·04	3·4954	4·471
343·04	3·4722	4·442
348·02	4·9768	6·349
353·00	9·2361	11·54

The collision diameter (8·56 Å) for PI_3 was evaluated from the diameter of the minimum circumscribing sphere including the van der Waals' radii of the iodine atoms. For P_2I_4, the I–I internuclear distance via the inversion centre plus twice the van der Waals' radii was set equal to the collision diameter (9·85 Å). Crystallographic data were used for bond lengths[8, 9]. These are rather crude estimates of collision diameter but the approximation is unlikely to affect markedly the sublimation enthalpies as the sensitivity of the correction is *ca.* −0·05 kcal. mole^{-1} Å^{-1}.

Analysis of the sublimate in isolated runs for both series revealed the theoretical quantity of easily-hydrolysable iodide and the theoretical I : P ratio. Hence, the possibility of thermal decomposition was excluded. For P_2I_4, confirmation of this point was obtained from thermogravimetric experiments when no decomposition below the melting point was observed. The correction for the conversion of the P_2I_4 data from the reference temperature of 340 to 298·15 K was assumed to be within the experimental limits of error. Least squares analysis gave

$$\Delta H[PI_3, c \rightarrow g]298 = 15{\cdot}21 \pm 0{\cdot}86 \text{ kcal.mole}^{-1}$$
$$\Delta H[P_2I_4, c \rightarrow g]298 = 16{\cdot}70 \pm 0{\cdot}50 \text{ kcal.mole}^{-1}$$

The precision of these data are nearly an order of magnitude less than that obtained by Kington and Edwards or Andrews and Westrum using similar equipment. This is possibly due to the necessity of fabricating the cell in stainless steel, a relatively poor thermal conductor.

DISCUSSION

The functional dependence of material loss from an effusion cell and equilibrium vapour pressure, under ideal conditions of infinitely thin edges to the orifice and a large mean free path to orifice diameter ratio (λ/d), was first derived by Langmuir[10]. In the present work an equation containing correction factors for an orifice of finite length (Knudsen)[11] and a non-ideal λ/d ratio (Hiby and Pahl)[12] is used. Notwithstanding these corrections, vapour pressures via Knudsen effusion techniques are often found to be dependent on orifice size[13]. However, the slope of the $\ln p$ vs. T^{-1} line (and hence $\Delta H[c \rightarrow g]$) is independent of this factor[14]. No attempt was made in this work to study the effect of orifice diameter and hence the quoted pressures are less significant than the derived sublimation enthalpies.

The bond energies in the phosphorus iodides are derived as follows, all thermochemical data being quoted at 298·15K. Head has recently reported a definitive value for $\Delta H_f^0[H_3PO_4 \cdot 40H_2O]$ (= 309·39 ± 0·24 kcal.mole^{-1}) [15]. Thus,

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using enthalpies of dilution from Ref. [16], $\Delta H_f^0[\mathrm{H_3PO_4 3000H_2O}] = -310{\cdot}18 \pm 0{\cdot}24$ kcal.mole^{-1}. Combination of this figure with the results of a thermochemical study of phosphorous acid oxidation[17] gives $\Delta H_f^0[\mathrm{H_3PO_3}, \text{cryst.}] = -228{\cdot}81 \pm 0{\cdot}3$ kcal.mole^{-1} and with dilution data[16], $\Delta H_f^0[\mathrm{H_3PO_3}\ \text{aq.}] = -228{\cdot}9 \pm 0{\cdot}3$ kcal.mole^{-1}. Combination of this latter datum with the results of a thermochemical investigation of PI_3 and P_2I_4[2, 18] gives $\Delta H_f^0[\mathrm{PI_3}, c] = -13{\cdot}9 \pm 0{\cdot}4$ kcal.mole^{-1} and $\Delta H_f^0[\mathrm{P_2I_4}, c] = -26{\cdot}5 \pm 0{\cdot}8$ kcal.mole^{-1}. Using the sublimation enthalpies derived earlier, we have $\Delta H_f^0[\mathrm{PI_3}, g] = +1{\cdot}3 \pm 0{\cdot}9$ kcal.mole^{-1} and $\Delta H_f^0[\mathrm{P_2I_4}, g] = -9{\cdot}8 \pm 0{\cdot}9$ kcal.mole^{-1}. Taking $\Delta H_f^0[\mathrm{P}, g] = 75{\cdot}20$ 16], and $\Delta H_f^0[\mathrm{I}, g] = 25{\cdot}535$[16] kcal.g.atom^{-1} we may readily derive the mean bond dissociation energy in $PI_3(\bar{D}(\mathrm{P{-}I}) = 50{\cdot}2$ kcal) and assuming that $\bar{D}$ in PI_3 may be set equal to the phosphorus–iodine bond energy (E(P–I)) in P_2I_4, a value of 61·7 kcal for E(P–P) follows. The overall uncertainty in these bond strengths is *ca.* 2 kcal. This value may be compared to other determinations of E(P–P); 51[19], 47 (in P_2H_4)[20], 67 (in P_2I_4)[21] and corresponding determinations of D(P–P); 58 (in P_2Cl_4)[22], 65 (in P_2I_4)[23], 86 (in $(C_2H_5)_4P_2$)[24], and 74 (in P_2H_4)[25] kcal.mole^{-1}.

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The Phosphorus–Phosphorus Bond: some Electron Impact Studies

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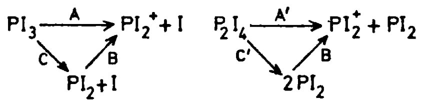
PHYSICAL data concerning the P–P bond, even in very simple systems, are scarce. From some detailed mass spectroscopic studies of both phosphorus tri-iodide and diphosphorus tetraiodide,[1] an estimate of the strength of the P–P bond may be made. Relevant results are shown in the cycles:



The appearance potentials for processes A and A′, are 11·9 ±0·15 and 12·8±0·15 ev respectively. If the literature[2] value for the energy of the dissociation process C, 184·1 kJ mole^{-1} (44 kcal. mole^{-1}), is adopted, then the bond dissociation energy $D(PI_2–PI_2)$ (process C′) is 271·0 kJ mole^{-1} (64·8 kcal. mole^{-1}). This is in excellent agreement with a previous estimate,[3] 269·9 kJ mole^{-1} (64·5 kcal.mole^{-1}) and also with two values, 263·6 and 217·6 kJ mole^{-1} (63 and 52 kcal.mole^{-1}) derived from a mass spectroscopic study[4] of PCl_3 and P_2Cl_4 for D $(PCl_2–PCl_2)$. Cracking patterns for the chloride[4] and iodide[1] systems differ considerably and in the former the appearance potential of PCl_2^+ from PCl_3 exceeds that of the appearance potential of PCl_2^+ from P_2Cl_4, in contrast to the above results (processes A, A′).

In both chloride and iodide systems the value corresponding to process C was estimated as one third of the heat of formation of PX_3 with respect to the gaseous elements *i.e.* with the implicit assumption that $D(PX_2–X) = \bar{D}(P–X)$. This is known to be invalid for other Group V molecules, *e.g.* NF_3, NH_3; hence a third experimental result of this investigation, a value of 12·7 ± 0·15 ev for the appearance potential of I^+ from PI_3 is relevant. On the assumption that this results from the process

$$PI_3 + e \rightarrow PI_2 + I^+ + 2e,$$

use of the value[5] of 10·45 ev for the ionisation potential of iodine, gives $D(PI_2–I) = 217$ kJ.mole^{-1} (52 kcal.mole^{-1}) and $D(PI_2–PI_2) = 309$ kJ.mole^{-1} (73 kcal.mole^{-1}).

Since all values for the phosphorus–iodine bond strengths have previously relied on assumed values of ΔH°_{vap} PI_3 or P_2I_4, the latter values are entirely reasonable. Hence they may now be used to estimate the heats of sublimation. Direct determination of these is extremely difficult, owing to the very low vapour pressures at ambient temperatures and thermal instability at elevated temperatures. However, experimental studies, with Knudsen-type and thermal conductivity gauges are in progress.

Appearance potential measurements were performed by use of an AEI model MS2H mass spectrometer with a direct inlet system for solid samples of PI_3 and P_2I_4; the method of Lossing *et al.*[6] was used, with argon as internal standard.

(*Received, February 13th,* 1969; *Com.* 198.)

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The Disproportionation of Phenyldifluorophosphine

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Summary Polymeric phenylphosphines are formed on spontaneous disproportionation of phenyldifluorophosphine under nitrogen at room temperature.

ANG and SCHMUTZLER[1] recently reported the spontaneous disproportionation of phenyldifluorophosphine to pentaphenylpentaphospholan and phenyltetrafluorophosphorane:

$$10PhPF_2 \rightarrow 5PhPF_4 + (PhP)_5$$

While the constitution of all forms of the phenylphosphines, $(PhP)_n$, is not established,[2,3] it is agreed that at least three species exist: Form A ($n = 5$, m.p. 149—150°), Form B ($n = 6$, m.p. 190°), and at least one (presumed polymeric) form of unknown molecularity which melts within the range 252—285°, and is insoluble in organic solvents. Henderson *et al.*[4] have distinguished two high melting forms, C and D, melting within the ranges 270—283° and 260—285°, respectively.

On the basis of observed melting point (151—154°), and comparison of the *X*-ray diffraction pattern with that of an authentic sample, Ang and Schmutzler[1] report that the disproportionation product is the pentamer, Form A. However, this disproportionation was observed in these laboratories some years ago,[5] and has been re-checked recently. Both phenyldifluorophosphine, and an equimolar mixture of phenyldifluorophosphine and phenyldichlorophosphine, allowed to stand at room temperature under nitrogen, deposit a white powder, insoluble in organic solvents, which melts near 280°. This clearly indicates the production of a polymeric form, probably D,:

$$2PhPF_2 \rightarrow \frac{1}{n}(PhP)_n + PhPF_4$$

and not A, as found by Ang and Schmutzler.[1] Samples of our product re-melted at 150°, and were then soluble in organic solvents, as previously noted elsewhere[6] for D.

An *X*-ray diffraction pattern for our product further confirmed that it was not Form A, but was markedly similar to the corresponding (identical) patterns[7] obtained for authentic samples of Forms C and D, although minor differences in both intensities and line sequence were noted.

There is at present no reproducible synthetic route[2,4] to the polymeric phenylphosphines. Although interconversion from Form A, (which is readily prepared) to Form C *via* warming in piperidine at 80° has been reported,[3] we have had little success with this procedure. Hence direct formation of a polymeric form from the above disproportionation represents a simple synthesis from readily available precursors.

Identical samples of polymeric phenylphosphine were obtained from disproportionation experiments of very different time-span (2 days and some months). It is therefore difficult to reconcile the difference in product obtained in these experiments and those reported earlier.[1] However, it seems clear that the polymeric form(s) is thermally unstable with respect to the pentamer, and lack of synthetic reproducibility is apparently[4] a feature of these systems.

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